

# **Residence Time Distribution modeling of combustors through Chemical Reactor Network**

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### **English translation for information purposes only:**

I herewith declare that I have written the submitted dissertation independently, except for explicitly quoted sources. I furthermore declare that I have not applied for a PhD before.

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Darmstadt, 16. April 2019

Maria Angela Agizza, M.Sc.



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# Nomenclature

## Abbreviations

CARS	Coherent Anti-Stokes Raman
CM	Compartmental Model
CRN	Chemical Reactor Network
CSTR	Continuous Stirred Tank Reactor
ERZ	External Recirculation Zone
IRZ	Internal Recirculation Zone
LIF	Laser Induced Fluorescence
OFC	OxyFuel Combustor
PFR	Plug Flow Reactor
RTD	Residence Time Distribution
RZ	Recirculation Zone
SSGT	Single Sector Gas Turbine model combustor
<i>st.</i>	Staging ratio

## Greek notations

$\varphi$	Equivalence ratio
$\sigma^2$	Spread of a distribution
$\tau$	Mean residence time or space-time

## Roman notations

P	Pressure
S	Swirl number
$S^3$	Skewness of a distribution
T	Temperature



# German abstract

**Schlüsselwörter:** Verweilzeitverteilung, Chemical Reactor Network Modellierung, magere Verbrennung, Oxyfuel-Verbrennung.

Sowohl die Zunahme des Luftverkehrs als auch des Energiebedarfs erfordern eine kontinuierliche Verbesserung von Verbrennungskraftmaschinen, um die Nachhaltigkeit des Verbrennungsprozesses sicherzustellen. Um die Verbrennungseffizienz zu erhöhen und die Schadstoffemissionen zu reduzieren werden neue Verbrennungskonzepte vorgeschlagen und getestet.

Die magere Verbrennung erfüllt die Anforderungen eines effizienten und sauberen Verbrennungsprozesses für Luftfahrtgasturbinen. Sie ist oft mit einer Effusionskühlung der Brennkammerwände gekoppelt. Dabei ist die Wechselwirkung zwischen einer heißen Reaktionsumgebung und einer kalten Kühlluft noch nicht vollständig verstanden. Diese muss weiter untersucht werden, da aufgrund einer schnellen und inhomogenen Abkühlung von reagierenden Fluideinschlüssen hohe Kohlenmonoxidemissionen entstehen können.

Die Oxyfuel-Verbrennung ist stattdessen eine Strategie, die für stationäre Kraftwerke anwendbar ist. In diesem Fall erfolgt eine Substitution von Luft durch ein Gemisch aus Kohlenstoffdioxid und Sauerstoff. Dies stellt eine Neuheit in Bezug auf die Standardverbrennung in Luft dar, wodurch ein besseres Verständnis der Auswirkungen von überschüssigem CO<sub>2</sub> in einer Reaktionsumgebung entscheidend ist. Zu diesem Zweck ist eine gründliche experimentelle Untersuchung in einer entsprechend realitätsnahen Konfiguration erforderlich, die idealerweise durch die Modellierung der beobachteten Phänomene ergänzt wird. Eine Modellierungsstrategie, die gut zu der Idee einer starken Synergie zwischen Experimenten und Modellierung passt, wird als “Chemical Reactor Network” (CRN) Modellierung bezeichnet. Bei dieser Vorgehensweise wird eine vereinfachte Form des Strömungsfeldes betrachtet, basierend auf zwei extremen Mischungsmöglichkeiten. Diese Modelle werden häufig gegen die Verweilzeitverteilung einer bestimmten Konfiguration bemessen, welche bereits wertvolle Informationen über die Mischcharakteristik des untersuchten Systems liefert.

In der vorliegenden Arbeit wird die CRN-Modellierung für zwei entsprechend realitätsnahe Umgebungen angewendet. Sie sind repräsentativ für die Brennkammer einer Luftfahrtgasturbine und einer Kraftwerkfeuerung. Diese Konfigurationen wurden entworfen, um die zugrunde liegenden Phänomene besser zu verstehen und gleichzeitig neue Verbrennungskonzepte zu untersuchen, nämlich die magere Verbrennung bzw. die Oxyfuel-Verbrennung. Ein CRN-Modell wird jeweils für die beiden Situationen entwickelt und getestet. Diese basieren auf der zonalen Modellierung des Strömungsfeldes und der Verweilzeitverteilung der Systeme.

Für beide Fälle wird die Leistungsfähigkeit anhand zur Verfügung stehender experimenteller Daten getestet. Außerdem werden sie verwendet um die Auswirkungen der Betriebsbedingungen auf den Verbrennungsprozess besser zu verstehen.

In dieser Arbeit wird die Wichtigkeit solcher einfachen und flexiblen Werkzeuge für die Verbrennungsforschung aufgezeigt.





# English abstract

**Keywords:** Residence Time Distribution, Chemical Reactor Network, Lean Combustion, Oxyfuel Combustion.

The growing globalization and continuous industrial and urban development result in an ever-increasing energy demand for transportation and power generation. Therefore, providing sustainable and clean conversion processes is one of the most crucial challenges worldwide. By virtue of the high energy density of chemical fuels and the capability of satisfying strongly fluctuating energy demand, combustion dominates the global energy scenario. According to the crucial reasons listed above, its importance is not diminishing in the foreseeable future, despite the increasing share of renewable conversion sources. Hence, a continuous improvement of combustion devices, to increase their efficiency and reduce pollutants emission, is mandatory, and new combustion concepts must be explored and tested.

Lean combustion fulfills the requirements of an efficient and clean combustion process, applicable to aviation gas turbines. As it results in higher temperatures of the combustor wall, this process is often coupled with effusion cooling of the combustor liner. This poses the problem of the interaction between a hot reactive environment and cold cooling air, which is not yet fully understood. This strategy needs further investigation because it could lead to high carbon monoxide emissions due to rapid and inhomogeneous cooling of pockets of reacting fluid.

Oxyfuel combustion, instead, is a strategy applicable to stationary power plants. In this case, the substitution of air with a mixture comprising carbon dioxide and oxygen takes place. Such an approach represents a point of novelty with respect to standard combustion in air. Therefore, an improved understanding of the effect of excess  $\text{CO}_2$  in a reaction environment is crucial.

Both outlined technologies present undeniable advantages, yet their possible drawbacks need to be understood and avoided, and a deeper knowledge is required to properly exploit their potential. To this aim, thorough experimental investigation in suitably designed close-to-reality configuration is mandatory, and ideally complemented by the modeling of the observed phenomena.

A modeling strategy that well fits the idea of a strong synergy between experiments and modeling, is referred to as Chemical Reactor Network (CRN) modeling. This strategy proposes a simplified version of the flow field based on two extreme mixing possibilities. Such models give insight into the mixing and reactive features of a complex flow, as the ones encountered in practical combustion devices. To achieve a proper CRN model, it is possible to design and size it against the Residence Time Distribution (RTD) of a certain configuration. Even without further modeling, RTD data alone yields precious information on the mixing characteristic of the system under investigation.

In the current work, Chemical Reactor Network modeling based on experimental Residence Time Distribution data is applied to two suitably designed close-to-reality configurations. They are representative of an aviation gas turbine combustor and a power generation furnace. These systems were designed to better understand the underlying phenomena while investigating new combustion concepts, such as lean combustion and oxyfuel combustion. CRN models are designed and tested in both situations. These models are developed based on zonal modeling of the flow field and on the Residence Time Distribution of the systems. In both cases, their performances are tested against experimental data available for both test-rigs regarding pollutants emissions. Additionally, they are employed to understand the impact of the operating conditions on the combustion process.

This work states the importance of such simple and flexible tools in combustion research.



# Italian abstract

**Parole chiave:** Distribuzione dei Tempi di Residenza, Modello a Compartimenti, Combustione Magra, Ossicombustione

La crescente globalizzazione e il continuo sviluppo industriale e urbanistico sono alla base di un continuo incremento della richiesta energetica per il settore dei trasporti e della produzione di elettricità. Perciò, fornire processi di conversione energetica sostenibile e a ridotte emissioni di inquinanti è una delle più grandi sfide a livello mondiale. Grazie alla elevata densità energetica dei combustibili e la flessibilità nel soddisfare richieste energetiche oscillanti, il processo di combustione domina lo scenario energetico globale e la sua importanza non diminuirà in breve tempo. Di conseguenza, il suo continuo miglioramento, al fine di aumentarne l'efficienza e ridurre le emissioni inquinanti, è di fondamentale importanza e nuove tecnologie devono essere proposte e testate.

Un processo di combustione caratterizzato da condizioni magre soddisfa i requisiti di efficienza e ridotte emissioni, applicabile alle turbine a gas di tipo aeronautico. Un inconveniente di questo processo è l'aumento della temperatura di parete all'interno del combustore. Pertanto, la combustione magra è spesso accoppiata a un raffreddamento di tipo ad effusione del rivestimento della superficie del combustore. Ciò costringe a fronteggiare il problema della complessa interazione tra l'ambiente di reazione estremamente caldo e la corrente di aria fredda adibita al raffreddamento, che non è ancora pienamente compresa. Per questo motivo, ulteriori studi sono necessari in quanto una tale condizione operativa potrebbe portare alla produzione di elevate emissioni di monossido di carbonio come conseguenza di un rapido e disomogeneo raffreddamento di sacche di fluido reagente.

D'altro canto, per quanto riguarda le grandi centrali elettriche, l'ossicombustione (Oxyfuel) rappresenta una valida strategia caratterizzata dalla sostituzione di aria con una miscela formata da anidride carbonica e ossigeno. Tale approccio costituisce una novità rispetto alle metodologie di combustione standard e, a tal riguardo, è quindi fondamentale ottenere una migliore comprensione degli effetti dovuti alla presenza di un eccesso di  $\text{CO}_2$  in un ambiente reagente.

Le due tecnologie descritte hanno vantaggi innegabili. Tuttavia, gli eventuali inconvenienti che possono derivarne devono essere compresi ed evitati. È, pertanto, fondamentale perseguire approfondite indagini di tipo sperimentale in apparati il più possibile realistici, le quali devono inoltre essere affiancate e completate da modellazioni di tipo numerico dei diversi fenomeni osservati. In tale contesto, una strategia che ben si adatta all'idea di questa forte sinergia tra ricerca sperimentale e investigazione numerica è rappresentata dalla cosiddetta tecnica di modellazione "Chemical Reactor Network" (CRN, detto anche "modello a compartimenti"). Questo approccio propone una versione semplificata del campo di moto, basata sulle due possibilità estreme di miscelazione. Modelli di questo genere consentono di approfondire la comprensione delle proprietà reattive e di micelazione di campi di moto complicati, come quelli che caratterizzano i dispositivi di combustione reali. Questi modelli sono spesso dimensionati rispetto alla "Residence Time Distribution" (distribuzione del tempo di residenza) di una determinata configurazione. Questa quantità consente inoltre di ottenere preziose informazioni sulle caratteristiche di miscelazione del sistema in esame anche in assenza di modellazione dei dati.

Nel presente lavoro, la metodologia basata sul modello a compartimenti viene applicata a due configurazioni, appositamente progettate per rispecchiare condizioni di funzionamento reali, rappresentate rispettivamente da un combustore di turbina a gas per aeromobili e un forno dedicato alla produzione di potenza. Questi sistemi sono stati realizzati per comprendere al meglio i fenomeni alla base dei nuovi approcci menzionati. In entrambi i casi, modelli di tipo CRN sono stati progettati e testati. Tali modelli sono sviluppati sulla base di una riproduzione di tipo zonale del campo di moto e della distribuzione dei tempi di residenza. I risultati ottenuti dai modelli sono confrontati con i set di dati sperimentali disponibili per entrambi gli impianti. Inoltre, i risultati ottenuti sono utilizzati per comprendere l'impatto che le condizioni operative esercitano sulla fase di combustione. Questo lavoro afferma l'importanza che tali semplici e flessibili strumenti rivestono per un'attività di ricerca relativa ai processi di combustione.



# 1 Introduction

The continuous improvement of combustion-based devices is of paramount importance for environmental and economic reasons. This urgency stems from the increased usage of aviation transportation and energy demand, based on the population and economic growth. In this scenario, to keep the present pace and be able to keep up with future requirements, the growth trend needs to be backed up by the sustainability of the process [1].

The optimization of the combustion process is, nonetheless, far from trivial. It must consider two different aspects, often in opposition with each other: great enhancement of combustion efficiency and drastic reduction of pollutant emissions. The need for process efficiency is driven by economic and political reasons, linked to the availability of the fuel resources. The reduction of emissions from harmful pollutants is mandatory and strictly regulated by environmental organizations. Indeed, these regulations become more and more stringent over the years. The most important and regulated pollutants are carbon monoxide (CO), nitrogen oxides (NO, NO<sub>2</sub>), widely known as NO<sub>x</sub>, unburned hydrocarbons (UHC) and particulate matter. On the other hand, CO<sub>2</sub> is not considered a direct pollutant, but its emission must be reduced because of the role it plays on global warming [2].

Therefore, the present and well-established combustion processes must be continuously improved, whereas new combustion concepts must be as well explored [3].

There are few options to achieve the goals listed above, both for aviation engines and for stationary devices for power generation.

Lean combustion emerges as an extremely promising strategy to keep the promise of an efficient and clean combustion process, applicable to aviation gas turbines [4], [5]. The peak temperature of the process is lower with respect to the established technology, thus reducing the formation of thermal NO<sub>x</sub>. Furthermore, lean combustion allows, in theory, to entirely consume the fuel fed to the combustor and to drastically reduce hydrocarbons and CO emission. Due to the increasingly stringent regulations on pollutant emissions, aircraft engine companies are pushing the research and development on lean technologies. However, further investigations are necessary to successfully implement this strategy. An issue that accompanies the presented technology is the higher thermal stress on the combustor walls: it stems from a lower availability of cooling air because more air is fed via the reaction airflow to achieve a leaner mixture. To adequately face this problem, smarter cooling technologies have been developed. Among others effusion cooling proves to be one of the most effective, being able to provide adequate cooling protection despite the lower available amount of air [6]. The introduction of air along the combustor walls presents, however, a drawback: it poses the problem of the interaction between a reactive flow and cold air. This chance is enhanced in small combustors, whose downsizing is driven by market requirements. In this context, carbon monoxide production becomes a pressing issue. In an ideal combustion process, CO is an intermediate species and should react further to form carbon dioxide (CO<sub>2</sub>). This transformation is slower compared to the main combustion reactions and requires adequate residence time at high temperature. In this context, the mixing of hot combustion products with cooling air introduced along the combustor wall could indeed quench the reactions. Therefore, further studies are needed to fully understand the implications of the interaction between a high temperature reactive environment and cooling air.

A combustion process applicable to combustion devices for stationary power generation is oxyfuel combustion [7]. In this concept, a mixture of carbon dioxide (CO<sub>2</sub>) and oxygen replaces air, leading to an exhaust gas mainly composed of water vapor and enriched in CO<sub>2</sub> formed by fuel combustion. The CO<sub>2</sub> can be separated, liquefied and stored underground to reduce the effects on the environment. This strategy is gaining increasing attention in recent years because of its suitability in the view of carbon capture and storage technologies [8]: beside the high CO<sub>2</sub> content of reactive mixture, it allows the existing power plants to be adapted to this process, with a lower expense that would derive to implement completely new energy production technologies. The issue here lies in the testing needed to understand the interactions and implications of a reacting environment that is different from what has been studied

so far.  $\text{CO}_2$  has a higher specific heat capacity with respect to nitrogen ( $\text{N}_2$ ), determining a different global temperature in the system. Furthermore,  $\text{CO}_2$  is one of the main combustion products, and its presence in the system influences the overall combustion kinetics.

As pointed out, these two new combustion concepts are proposed and explored, yet the implications and potential of those concepts are not fully understood. The development and testing of new processes, as well as the improvement of present technologies needs thorough experimental investigations on properly designed laboratory scale model combustors. To this aim, comprehensive experimental investigations on appropriate close-to-reality configurations are crucial to deepen the understanding of the underlying interactions occurring during the combustion process. These configurations allow considering all the complexity that characterizes real scale processes, though on a smaller scale. Ideally, the modelling of the processes involved supports the interpretation of experimental results. Although computational fluid dynamics (CFD) is nowadays a valuable tool, it is, however, computationally costly especially if detailed kinetic mechanisms are considered. Therefore, a somewhat simpler and more flexible tool is needed.

A reactive flow modelling that fits these needs is referred to as Chemical Reactor Network (CRN). It employs a properly designed arrangement of ideal flow reactors to obtain a simplified version of the flow field inside a generic combustor. This simplification allows for the use of detailed kinetic mechanisms. A properly designed Chemical Reactor Network enables quantitative species concentrations extraction, making parametric studies possible. This modeling strategy exploits the Residence Time Distribution (RTD) of the flow, that yields the mixing characteristics, which must be reproduced in order to properly describe the reactive flow.

In the present study, to shed light on the underlying phenomena characterizing the above-mentioned combustion concepts, two close-to-reality configurations are thoroughly investigated by Residence Time Distribution measurements. The experimental data are exploited to model the configurations designing a Chemical Reactor Network.

## 1.1 Aims and Structure of the Work

In the present study, two close-to-reality configurations that exemplify the combustion systems mentioned above are investigated by Residence Time Distribution measurements followed by Chemical Reactor Network modeling.

The technologies described earlier, namely the employment of an effusion cooling liner and the oxyfuel process, are crucial for the optimization of the systems devoted both to transportation and energy production. Therefore, the aim of this work is to improve the understanding of combustion-based devices that apply these technologies. A deeper knowledge about the investigated configurations is achieved by designing a Chemical Reactor Network of the experimental facility at hand and calibrating it against the measured Residence Time Distribution of the system. Residence Time Distribution is a meaningful quantity to measure to assess the macro-mixing characteristics of a generic reactor, whereas Chemical Reactor Network modeling enables the investigation of the reactive feature of a complex system properly schematized in a simpler way. By coupling these two investigation strategies, an improved understanding of the interaction between mixing and chemical reaction is gained.

The work develops as follows.

- The next paragraph of this chapter is dedicated to the fundamentals of combustion and combustion features in real configurations. The last section of this chapter is concerned about the modeling strategies applied to combustion. Here, more details are provided to motivate the modeling that has been applied in this work.
- Chapter 2 introduces the basics of RTD theory and modeling. After the basics of RTD theory, the tools and procedures employed in this work are presented. An overview of the different Chemical Reactor Network modeling strategies is provided, and the novelty of the present approach better evidenced.

- Chapter 3 contains the work carried out on the Single Sector Gas Turbine (SSGT) model combustor. This configuration allows the investigation of the interaction between a reactive flow operated in the lean combustion regime and an effusion cooling air, dealing with a pressing issue relevant for aviation gas turbines. The test rig is described, together with the RTD measurements setup. The experimental results are briefly shown, before a deep explanation of the model development. The models are then fit to the measurements and sensitivity analysis and error analysis are provided. Follows a description of the CRNs and the comparison between the calculated results and the available experiments in terms of species formation. Finally, the model is applied to several operating conditions to extract the features that characterize each one of them both from a mixing and reactive point of view.
- Chapter 4 is dedicated to an experimental apparatus that is conceived to mimic the most important features of power plants combustors applying the oxyfuel combustion technology, the OxyFuel Combustor (OFC). In this case, RTD data from a previous measurement campaign are exploited. Therefore, after showing the experimental apparatus, the designed networks are introduced, and their performance evaluated. The calculated species formation is compared to available experiments to assess the validity of the network models. There follows a section commenting on the impact of the operating atmosphere in the case of non-reactive and reactive flow.
- Chapter 5 summarizes the work.

## 1.2 Combustion Fundamentals

The word “combustion” refers to the reaction between a fuel and an oxidizer that proceeds toward the oxidation of the fuel. As only gas phase combustion is addressed in this work, all the concepts reported in the following refer to combustion of gas species, i.e. single phase multicomponent reactive flow. The reaction is highly exothermic and requires a high activation energy. During the oxidation reactions, the bonds between the fuel molecules and those between oxidizer molecules are broken with release of energy to the surrounding fluid. The formal equations to treat the evolution of a generic multicomponent reactive system, in the hypothesis of homogeneity of the system itself, are provided in the following, Equation 1-Equation 4 . The aim is to describe how such systems are approached from an analytical point of view, and a deeper description is found in [9]–[11].

<b>Mass balance</b>	$\frac{\partial \rho}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v}) = 0$	<i>Equation 1</i>
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$\rho$ : density, $kg/m^3$ $\underline{v}$ : velocity, $m/s$	$\underline{\nabla}$ : divergence
---	-----------------------------------

<b>Mass balance for each species “i”</b>	$\frac{\partial(\rho Y_i)}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v} Y_i) + \nabla \cdot J_{Y_i} = \dot{\rho}_i$	<i>Equation 2</i>
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$Y_i$ : mass fraction of species “i” $\dot{\rho}_i$ : production of species “i”	$\nabla$ : gradient
--	---------------------

<b>Momentum balance</b>	$\frac{\partial(\rho \underline{v})}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v} \underline{v}) + \nabla \cdot J_v = -\underline{\nabla} p$	<i>Equation 3</i>
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$\nabla$ : gradient $J_q$ : diffusive flux associated with quantity “q”	
--	--

<b>Energy balance</b>	$\frac{\partial(\rho h^s)}{\partial t} + \underline{\nabla} \cdot (\rho \underline{v} h^s) + \nabla \cdot J_{h^s} = \sum_i \dot{\rho}_i h_i^0$	<i>Equation 4</i>
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$h_i^0$ : enthalpy of formation of species “i”

$h^s$ : sensible contribution to the enthalpy of the system

$$h^s = \sum_i \dot{\rho}_i \int_{T_{reference}}^T c_{p_i}(T) dT$$

Equation 5

$c_{p_i}$ : sensible heat of the system

### 1.2.1 Turbulent flow fields

The main characteristic of a turbulent flow field is the irregularity of its evolution over time. Beside this strong irregularity, these flow fields show high diffusivity of extensive quantities and are intrinsically three dimensional. Furthermore, they are highly dissipative, meaning that the kinetic energy of the flow is converted, through an energy cascade from large scale of motion to smallest eddies, responsible for viscous dissipation, into internal energy. The mentioned high diffusivity of extensive quantities makes this flow attractive for practical applications: when turbulent flows are applied to combustion, mixing is enhanced. However, given the complexity of the situation, the coupling between the equations Equation 1-Equation 4 makes it impossible to achieve an analytical solution of the system of equations for such flows.

A flow is classified turbulent or laminar based on its Reynolds number [12]:

$$\Re = \frac{\rho v l_0}{\mu}$$

Equation 6

$\rho$ : density,  $kg/m^3$

$v$ : characteristic velocity, m/s

$l_0$ : characteristic length, m

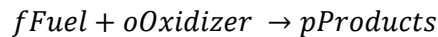
$\mu$ : dynamic viscosity,  $Pa \cdot s$

For  $\Re > 4000$ , turbulent flows are identified.

Eddies of different size compose turbulent flows, according to [13]. The maximum size of these eddies coincides with the integral length scale of the problem,  $l_0$ . The big eddies undergo a break-up process, forming smaller eddies distributed among several different length scales. Energy is transferred from the bigger to the smaller length scales, until the dissipation region, where the energy is dissipated and not transferred further [14]. Based on this concept, two characteristic domains of scales are identified: the integral time and length scales ( $\tau_0$  and  $l_0$  respectively, that are highly dependent on the flow), and the Kolmogorov time scales ( $\tau_k$  and  $l_k$ ). The latter are the smallest identified scales before viscous dissipation occurs instead of energy transfer.

### 1.2.2 Chemical kinetics

Considering a generic fuel reacting with an oxidizer to form combustion products, the reaction is written as follows:

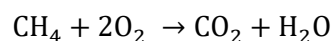


Reaction 1

Reaction 1 indicates that  $f$  moles of fuels react with  $o$  moles of oxidizer to form  $p$  moles of products.

In this work the operating fuel is natural gas, schematized as methane,  $CH_4$ . The choice of investigating natural gas-fueled test rigs follows the trend developed in the last years, that aims at increasing the use of natural gas as operation fuel, for its large availability and the chance to reduce  $CO_2$  emissions. In this context, more studies on close-to-reality configurations based on this fuel are needed to answer the questions related to the optimization and improvement of natural gas-fueled facilities

Considering  $CH_4$ , Reaction 1 is written in a more specific way as Reaction 2:



Reaction 2



Reaction 2 is a global reaction: it describes a process but behind it there is a huge number of elementary reactions [15]. The ensemble of elementary reactions behind a combustion process defines the kinetic mechanisms. For each elementary reaction, a rate coefficient is following an Arrhenius approach:

$$k = k_0 T^\beta e^{\left(\frac{-E}{RT}\right)} \quad \text{Reaction 3}$$

$k_0$ : pre-exponential factor

$E$ : activation energy

$R$ : universal gas constant

$\beta$ : temperature exponent

A crucial parameter in combustion processes is the amount of available oxidizer with respect to the fuel quantity, that defines the stoichiometric conditions of the mixture. If the amount of oxidizer is less than the one necessary to achieve complete fuel burnout, the combustion process is said to be rich. If the amount of oxidizer is more than the one necessary to achieve complete fuel burnout, lean conditions are established. When the amount of oxidizer is exactly the one required to ensure complete consumption of the fuel, the reactive mixture is in stoichiometric conditions. To describe the conditions of a reactive system in terms of stoichiometry, a parameter is used, called equivalence ratio,  $\varphi$ :

$$\varphi = \frac{m_{\text{fuel}}/m_{\text{oxidizer}}}{(m_{\text{fuel}}/m_{\text{oxidizer}})_{\text{stoichiometric}}} = \frac{n_{\text{fuel}}/n_{\text{oxidizer}}}{(n_{\text{fuel}}/n_{\text{oxidizer}})_{\text{stoichiometric}}} \quad \text{Equation 7}$$

$m$ : mass of a certain species, fuel or oxidizer

$n$ : number of moles of a certain species

### 1.2.3 Swirl combustion

Combustion stabilization in practical configurations is realized by imparting a spiraling motion to the flow entering the combustor. The implementation of this feature shortens the flame length (higher mixing rate), limits flame impingement on the combustor and enhances stability by triggering the formation of recirculation zones by means of vortex breakdown. The recirculation zones recirculate heat and chemical species sustaining the combustion process of the incoming fresh mixture [16], [17]. The degree of a tangential component impressed on the flow, referred to as degree of swirl,  $S$ , is defined as the axial flux of tangential momentum,  $G_{\text{tan}}$ , divided by axial flux of axial momentum,  $G_{\text{ax}}$ , times equivalent nozzle radius,  $R$ , Equation 8 [18].

$$S = \frac{G_{\text{tan}}}{RG_{\text{ax}}} \quad \text{Equation 8}$$

Peculiar features characterize swirling flows in confined configurations, as schematized in Figure 1.

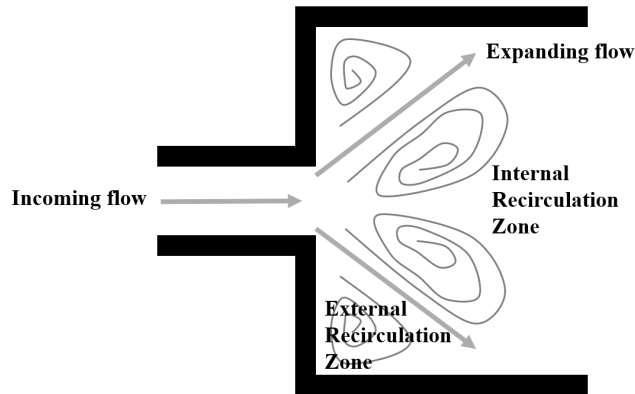


Figure 1: schematization of the main features of a swirling flow in a generic confined configuration. The configuration itself is sketched in black, the features of the swirling flow in grey.

The swirl imparted to the incoming flow is responsible for the formation of the recirculation zones indicated in Figure 1. These are responsible for flame stabilization by recirculating heat and reactive

species. Swirling flows are therefore crucial while adopting lean combustion strategies, where the risk of instabilities is high.

## 1.2.4 Pollutants formation

Several harmful pollutants are formed during the combustion process. The most important, and the ones that will be addressed in the following, are nitrogen oxides, carbon monoxide and soot. However, the latter will not be directly addressed, but rather a precursor, acetylene, will be discussed in the following work.

### 1.2.4.1 Nitrogen oxides

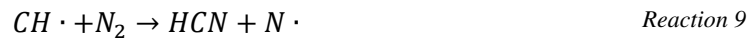
Several reaction pathways lead to the formation and emission of nitrogen oxides [19],  $\text{NO}_x$ .

- Thermal  $\text{NO}_x$ : oxygen radicals attack the atmospheric nitrogen, forming NO [20]. Relevant reactions are the following Reaction 4-Reaction 7:



Reaction 7 is clearly an important one because consumes the hydroxyl radical, that has a crucial role in CO oxidation to  $\text{CO}_2$  (more details below).

- Prompt  $\text{NO}_x$ : the formation of  $\text{HCN}$  is triggered by the attack from hydrocarbon radicals to atmospheric nitrogen. The relevant reactions listed below have been accepted in the research community as able to explain the observed phenomena.



$\text{HCN}$  and  $\text{CN} \cdot$  are easily oxidized to  $\text{NO}$ .

However, further research, [21], [22] among others, show that the following Reaction 11 is as important and better suited to explain the prompt NO production in flames.



The species formed during this reaction,  $\text{NCN}$ , is then responsible for NO formation under combustion conditions: NO can be formed readily by the rapid oxidation of  $\text{NCN}$  by  $\text{O}_x$  and  $\text{HO}_x$  ( $x = 1, 2$ ).

- Fuel  $\text{NO}_x$ : the nitrogen contained in the fuel is converted to nitrogen oxides.
- $\text{NO}_2$  formation. This transformation is a relatively slow one, and favoured below 1200 K.



Reaction 13 produces a highly reactive radical ( $\text{OH} \cdot$ ) starting from a weaker one ( $\text{HO}_2 \cdot$ ). For this reason, this reaction might be crucial for CO oxidation to  $\text{CO}_2$  in post-flame conditions [23].

- $\text{N}_2\text{O}$  formation. The reactions listed below acquire importance below 1500 K.



Reaction 15 is a termolecular reaction involving an entity (a third molecule or the enclosing walls) that is referred to as third body. This third body does not actively participate in the chemical transformation but is crucial from the energetic point of view. These reactions are favoured by higher pressures, compared to atmospheric conditions, because the higher pressure encourages third body reactions. Subsequently, this pathway is favoured at higher pressures.

### 1.2.4.2 Carbon Monoxide

Carbon monoxide is an intermediate species in the oxidation of hydrocarbon fuels to  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . Therefore, besides being a pollutant, it is also an indicator of fuel burnout. It is obviously present in fuel-rich combustion but should be in theory absent while adopting lean combustion. However, rapid cooling of reactive flow pockets or poor mixing cause high levels of CO to be produced also in overall lean applications. The significant reaction leading to  $\text{CO}_2$  from CO is:



This reaction is strongly affected by the temperature of the system, attribute to the temperature effect on equilibrium OH concentration [19].

### 1.2.4.3 Soot

Soot is a harmful pollutant produced in the form of carbonaceous nanoparticles. Crucial soot precursors are Polycyclic Aromatic Hydrocarbons (PAH) and ethyne or acetylene,  $\text{C}_2\text{H}_2$ . The latter is believed to be the dominant mass growth species, according to [24].  $\text{C}_2\text{H}_2$  comes from dehydrogenation of hydrocarbon fuels, its formation starts from the recombination of two methyl radicals [25] and is therefore formed in the first reaction stages. It is produced as an intermediate as the system evolves towards complete oxidation. Acetylene is also directly involved in CO formation through the global process:



Because of its involvement in soot formation,  $\text{C}_2\text{H}_2$  formation will be considered later in this work.

## 1.3 Combustion Modeling

As outlined before, the understanding of combustion in technically relevant configuration is crucial. However, this task is far from being trivial. Direct observation of the phenomena by means of thorough experimental investigations would be ideal, though not always possible in real configurations because of the costs and the large variety of processes involved. For this reason, close-to-reality configurations are designed, to allow considering features of real combustion-based devices in a controlled environment. An overview of experimental work carried out so far in close-to-reality configurations is given by [26]. Experimental work is ideally accompanied by numerical modeling of the processes involved: the modeling of the phenomena improves the understanding of the experimental results. Moreover, a strong interaction between experiments and modeling is essential, because experiments provide evidence to validate models, and predictive, robust and accurate models speed up the design phases of experiments, testing of new concepts and design of optimized real devices. Two numerical modeling strategies are briefly introduced in the following, widely employed nowadays: Computational Fluid Dynamics (CFD) and Chemical Reactor Network (CRN) modeling. Their strengths and weaknesses are highlighted, and the reasons why, in certain situations, one is chosen over the other is given.

### 1.3.1 Computational Fluid Dynamics

The basic concept of CFD is to solve a set of partial differential equations. The governing equations are the Navier–Stokes and continuity equations. According to [27], three different strategies are employed to carry out CFD simulations of combustion phenomena:

- Reynolds Averaged Navier Stokes (RANS)
- Large Eddy Simulations (LES)
- Direct Numerical Simulations (DNS)

These methods are listed in increasing complexity/computation cost order. They are based on a discretization of the domain (by applying a grid to the domain) in smaller control volumes, and the

balance equations are applied and solved in each control volume. The difference among the named methods concerns the different treatment of turbulent motions.

RANS models average in time the equations, and all the turbulence scales are modeled. This reduces the time required for a computation with respect to the other two methods (see below). When dealing with reactive flows in combustion, heavily simplified models are applied to incorporate chemical kinetics in the computation.

A turbulent flow field is separated in two scales while carrying out LES: a cut-off length is defined and referred to as filter size. Scales smaller than the length of the filter size are modeled using sub grid closure rules, whereas larger scales are calculated explicitly. Therefore, LES is more expensive than RANS from a computational point of view. Detailed chemical kinetics is not incorporated in this strategy because of the huge computational effort that it would imply, and several methods to deal with reactive flows have been developed and applied.

The two described computational methods operate with a heavily simplified version of the chemistry, taking advantage of several kinetic models suitable to be coupled with the calculation of the fluid dynamics of the system with a reasonable computational cost. Among others, the Flamelet model [28] is a well-known model to approach chemical kinetics in CFD. In this concept, a turbulent flame is treated as an aggregate of thin, laminar ( $\mathcal{R} < 2000$ , see section 1.2.1), locally one-dimensional flamelet structures within the turbulent flow field. This model is limited to flames with relatively fast chemistry that respond instantaneously to the aerodynamic strain, and thus does not capture deep non-equilibrium effects such as ignition, extinction, and slow chemistry. This last issue is crucial, because it prevents a correct prediction of  $NO_x$  production. The Eddy Dissipation Model [29] is another model widely incorporated in CFD codes. It is suitably applied when combustion is “mixing-limited” and the chemical reaction is governed by the mixing time scale of large eddies. This model has been found to work reasonably for non-premixed combustion, although it is not completely reliable for premixed combustion, as the reactants need some time to get to the ignition temperature and this is not considered in the model. The Eddy Dissipation Concept (EDC) [30] method is an extension of the eddy dissipation model that attempts to capture the role of fine structures in a turbulent reacting flow.

The reaction models that have been briefly reported, employed to deal with turbulent and reactive flow fields without implementing detailed kinetics, are not employed in Direct Numerical Simulation (DNS). DNS models explicitly calculate all the instantaneous heat and mass transport equations. In other words, all the turbulence scales of the flow are considered and solved. Moreover, detailed kinetics is incorporated in the model. This approach is the most expensive, among the three presented, from a computational point of view, making it impossible to employ it to model practical applications. This chance might be realized in the future, because of the upcoming increase in computational power.

The different CFD strategies and the methods to deal with the coupling of turbulent mixing and chemical reaction are treated in details, among others, in [27] and [31]. These strategies are capable of delivering detailed insights into the flow field characteristics and the combustion process itself. However, the two methods that can be exploited to model complex configurations, namely RANS and LES in virtue of the reasonable computational costs with respect to DNS, use a heavy simplification of the chemistry. Still, the most important features, specifically combustion efficiency and pollutant emissions of combustion-based devices, are determined by the complex interaction between turbulence and chemical reactions [32], [33]. Therefore, a somewhat simpler and more flexible tool is needed to incorporate chemical kinetics in the analysis of complex combustion devices.

### 1.3.2 Chemical Reactor Network modeling

The modeling of turbulent combustion makes an extensive use of Chemical Reactor Networks (CRNs), as will be comprehensively shown in the sections 2.3 and 2.4. Such models are based on dividing the combustor into multiple zones according to the identified mixing feature in the specific zone. The mixing characteristics are extremely simplified, and a combustor zone can be regarded as a perfectly mixed or

completely segregated one. The identified zones are then properly arranged in series or in parallel to yield a simplified description of the flow field. In each reactor of the network, the chemistry is solved with detailed kinetics. Compared to CFD models, the simplification of the fluid dynamic by adopting zone models with a well-defined mixing pattern lowers the computational demand by several orders of magnitude. In this regard, CRN models represent a valid reduced order alternative to incorporate detailed chemistry while investigating turbulent reactive flows. Hence, the understanding of the species formation pathways is achieved even in complex systems. The possibility to include detailed kinetic mechanisms into the analysis, still yielding severely lower computational effort with respect to CFD models, constitutes the main strength of this modelling strategy. On the other hand, the flow field is implemented indirectly, by inferring to a certain region inside the system a specific mixing behaviour rather than the other, and by connecting the zones in a certain way. In this sense, these reactor models are sometimes subjected to the experience of the user, although several precautions aid the design of a proper network.

Nonetheless, CRN models provide insight into the principal macroscopic mixing and reactive features of a generic complex system. They are indeed widely employed at the design stage of combustion based devices, to quickly estimate the response of a generic combustor to changes in design details or boundary conditions [34], [35]. The simplification of the flow field in zones with a defined mixing pattern allows a more direct link between setup modification and response of the system, linking it to macromixing pattern. Besides, reliable and validated CFD simulations of real and close-to-reality configurations are not easy to achieve. When this is the case, modelling the configuration under investigation using a CRN deepens the understanding of said configuration, helping to identify the crucial parameters influencing combustor performance. In this scenario, CRN models represent reduced order alternative to CFD simulation, with great potential to aid the design of improved combustors.

For this reason, this modelling strategy is extensively employed in this work to study the mixing and reactive characteristics of two close-to-reality configurations that simplify two pressing topics of combustion research: lean combustion coupled with effusion cooling for aviation gas turbines and oxyfuel combustion for stationary power plants. The different strategies that lead to the design of a CRN are described in chapter 2, together with a literature review about the results achieved by the various research groups adopting this methodology.



## 2 Chemical Reactor Network modeling

Chemical Reactor Network (CRN) modeling is employed in the following chapters to gain knowledge into the fundamental features that characterize combustion in technologically relevant experimental test rigs. There are several ways to apply this modeling strategy, outlined in the sections 2.3 and 2.4. In the present work, CRN modeling is achieved exploiting Residence Time Distribution (RTD) data of the flow in the enclosed environments under investigation. Therefore, a theoretical background on ideal flow reactors and basics on non-ideal flows is provided in the first part of this chapter, 2.1 and 2.2. Afterwards, an explanation of the methodology the tools employed is given. Follows a review of the application of the CRN modeling and the different ways to achieve it.

### 2.1 Ideal flow reactors

Before a brief description of the basic components employed to design a CRN, quantities relevant to chemical reaction engineering analysis are introduced.

A chemical reactor is a system where a chemical reaction takes place, transforming reactants into products. They are, in the first place, classified based on the type of process they fit in: batch or continuous. In this work, only continuous flow reactors are considered: reactants are fed into the process unit and emerge as continuous stream of product. This kind of process is usually run at steady-state.

The mass balance equation to calculate the conversion of a reactant feed stream in such a system is the generic:

$$\text{output} = \text{input} - \text{reacted quantity} \quad \text{Equation 9}$$

The term referring to the accumulated quantity, to be subtracted to the input, was omitted because only steady-state systems are treated.

The space-time [36] of a generic stream flowing through a reactor is defined as:

$$\tau = \text{time the system needs to process one unit of feed stream at the specified operating condition}$$

This quantity measures the advancement of a given reaction, given operating conditions and type of reactor. Thus, it depends on the reactor volume and the characteristics of the feed stream. In a generic situation, where

$A = \text{generic reactant,}$

$C_{A_0} = \text{concentration of the generic reactant A in the feed stream, [mol/m}^3]$

$V = \text{volume of the reactor, [m}^3]$

$F_{A_0} = \text{molar flow rate of reactant A entering the system, [mol/s]}$

$\dot{v} = \text{volumetric flow rate entering the system, [m}^3/\text{s]}$

$X_A = \text{degree of conversion of reactant A, [-]}$

$r_A = \text{volumetric reaction rate of reactant A, [unit depends on the reaction order]}$

the space time is calculated as:

$$\tau = C_{A_0} V / F_{A_0} = V / \dot{v} \quad \text{Equation 10}$$

#### 2.1.1 Continuous Stirred Tank Reactor

The Continuous Stirred Tank Reactor (CSTR), schematized in Figure 2, is the simplest flow reactor because it provides a 0D description of the flow and reaction pattern. The hypothesis behind it is that, as soon as the reactants enter the system, the mixing is so efficient that the concentration inside the system is spatially uniform and equals the concentration of the outgoing stream.

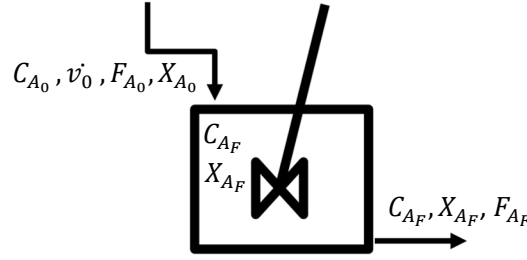


Figure 2: schematic of a Continuous Stirred Tank Reactor.

Because of the specific assumption of perfect mixing that is the foundation of this reactor, the terms of the general equation, Equation 9, is written as follows:

$$F_{A_0}(1 - X_{A_0}) = \text{input} \quad \text{Equation 11}$$

$$F_{A_0}(1 - X_A) = \text{output} \quad \text{Equation 12}$$

$$(-r_A)V = \text{consumed quantity} \quad \text{Equation 13}$$

And the space-time of the reactor is given by:

$$\tau = \frac{C_{A_0} V}{F_{A_0}} = \frac{V}{\dot{v}} = \frac{C_{A_0} X_A}{(-r_A)} \quad \text{Equation 14}$$

### 2.1.2 Plug Flow Reactor

The Plug Flow Reactor, or PFR (Figure 3), introduces complexities with respect to the previously presented reactor. It provides a 1-D description of the flow inside a system, and in this case the conversion of the reactants proceeds along the spatial coordinate, which is therefore also a reaction coordinate. This means that the concentration of each species varies along the length of the reactor. A plug flow is assumed, such that there is no back mixing of reactants and no possibility that a reaction product mixes with the unreacted, entering stream. However, along each cross section, perfect mixing on the radial coordinate is assumed.

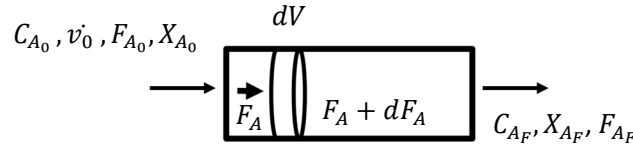


Figure 3: schematic of a Plug Flow Reactor.

Because of the basic hypothesis behind a PFR, Equation 9 should be solved for each control volume inside the system,  $dV$ . Therefore, for each  $dV$ :

$$F_A = \text{input} \quad \text{Equation 15}$$

$$F_A + dF_A = \text{output} \quad \text{Equation 16}$$

$$(-r_A)dV = \text{consumed quantity} \quad \text{Equation 17}$$

And the space-time of the reactor is given by:

$$\tau = C_{A_0} \int_{X_{A_0}}^{X_{A_f}} \frac{dX_A}{(-r_A)} \quad \text{Equation 18}$$

As stated before, and as proved by the absence of the accumulation term in Equation 9, the equation written up to now describe a steady state system, and no evolution over time is taken into account.



## 2.2 Residence time distribution

The two ideal flow reactors presented characterize two extreme mixing possibilities. To simplify the study of a certain system, a flow may be approximated either as fully mixed (CSTR) or completely segregated (PFR). Beyond a first simplification, real systems behavior is in between these two: there might be regions where complete mixing is an acceptable approximation, together with regions better described by plug flow. In addition, flow peculiarities such as dead volumes (stagnant regions that trap part of the flow inhibiting good mixing, Figure 4.a), or channeling of the flow (part of the flow that is accelerated to the exit of the reactor without having the chance to properly react, Figure 4.b) might as well take place, complicating the fluid dynamics of the system. In most cases, systems whose behavior can at a first glance be traced back to ideal systems, might undergo complex non-idealities, as shown in Figure 4.

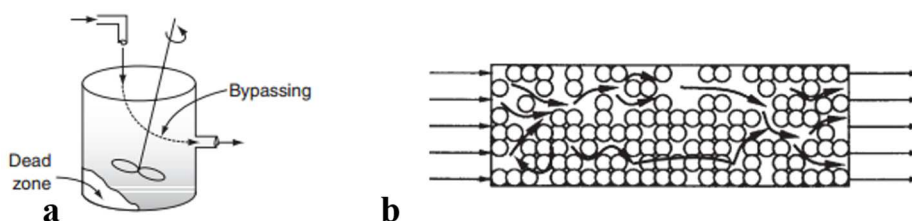


Figure 4: example of non-ideal flow in configurations that can be, in a first approximation, treated as ideal flow reactors, [36]. **a**, non-ideal CSTR; **b**, non-ideal PFR.

The study of real flow configurations gets more and more complicated the more information is needed for a good characterization. To approach this problem, it is necessary to focus on the basic information that allows reconstructing the fluid history inside a generic system. This is the distribution of residence times of the flowing fluid, i.e., the time the individual flow pockets spend inside the system. This distribution arises from the different lengths of time that different pockets of fluid take to pass in a flowing system where non-idealities of the flow occur: fluid particles that entered at the same time might not leave the reactor at the same time. For this reason, it is crucial to determine the Residence Time Distribution (RTD) of the flow [36]–[38], also represented by the notation  $E(t)$ , as for Exit Age Distribution.  $E(t)$  has units  $s^{-1}$ , and it is normally presented in its normalized form:

$$\int_0^{\infty} E(t) dt = 1 \quad \text{Equation 19}$$

In the following paragraph, the relevant aspects of Residence Time Distribution Theory will be briefly reviewed, according to [36]–[40].

The RTD of a system is determined experimentally, adopting the stimulus-response experiment: a certain amount of an inert tracer is introduced in one or all feed streams entering the reactor under investigation, with a defined input function. The temporal evolution of the concentration of this tracer in the stream exiting the reactor yields, directly or after mathematical treatment, the RTD of the reactor itself. In this way, the investigated system is treated as a black box: it is nothing more than a vessel with continuous fluid flow, as exemplified in Figure 5.

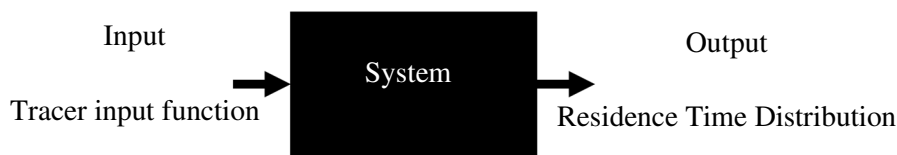


Figure 5: black box-treatment of a generic real system. An input is introduced in the system, and the output yields information on the intrinsic behavior of the system itself.

Adopting the described procedure, a perturbation, also referred to as disturbance, in the steady-state concentration of the system is introduced with a certain function over time. This perturbation propagates through the system experiencing its mixing features. The time-dependent concentration of the tracer at

the exit of the reactor differs from the one at the input. This difference is due to the peculiarities of the flow and mixing characteristics of the vessel: it is the result of the mixing pattern that occurs and enables to retrieve the transfer function of the system concerning its mixing behaviour. For the RTD to be a meaningful quantity to give insight into the global fluid dynamic of a generic reactor, it should respect the “closed-closed” vessel boundary condition: the flow can pass the boundaries, ideally conceived as detection stages as well, just once. In other words, there must be no risk of detecting the same pocket of fluid twice.

Several input schemes to inject the tracer can be considered [36], [39], but only two of them are detailed in the following because the other possibilities can be regarded as combination of the described two.

- Pulse input function: while adopting this injection strategy, a given amount of tracer is introduced at  $t = 0$  in the designated stream in a short time, ideally employing a Dirac-delta function,  $\delta(t)$ . As such a function is difficult to achieve in real experiments, while dealing with practical problems it is enough that the input pulse is significantly shorter than the mean residence time of the system under study. As the tracer passes through the system experiencing its mixing features, the peak of the concentration curve gets lower and its shape gets stretched: the resulting curve is referred to as the  $C_{pulse}$  curve. If a quantity  $M$ , expressed in kilograms or moles, of a tracer have been fed to a stream whose flow rate is  $\dot{v}$ , and the concentration over time exiting the system is  $C_{pulse}$ , the RTD is obtained from:

$$E(t) = C_{pulse}(t) / M / \dot{v} \quad \text{Equation 20}$$

As illustrated in Equation 20, the response of any system to a pulse input readily yields its RTD. For this reason, a pulse input is preferred, though its practical implementation is far from trivial. From the  $E(t)$ , the following global quantities are deduced:

$$\tau^m = \int_0^\infty t E(t) dt \quad \text{Equation 21}$$

$$\sigma^2 = \int_0^\infty (t - \bar{\tau})^2 E(t) dt \quad \text{Equation 22}$$

$$S^3 = \int_0^\infty (t - \bar{\tau})^3 E(t) dt \quad \text{Equation 23}$$

Equation 21 defines the mean residence time of a system,  $\tau^m$ . It indicates the mean of the distribution, and the time a pocket of fluid spends on average in the configuration. In an ideal situation it is the same as the space-time  $\tau$ , otherwise the two values differ due to flow non-idealities. Equation 22 calculates the variance of the distribution,  $\sigma^2$ , a measure of the spread of the curve. The skewness of the curve,  $S^3$ , is obtained by Equation 23. It quantifies the asymmetry of a distribution:  $S^3 < 0$  indicates a left skew distribution, right skew otherwise.

- Step input function: at  $t = 0$ , the concentration of the tracer in the inlet stream is suddenly increased to its final value and kept constant indefinitely. The transition from 0 to the final concentration value should be as fast as possible, ideally reproducing a Heaviside function. As the disturbance propagates through the system, the peak concentration gets lowered because of the mixing of the tracer. The outlet curve  $C_{step}$  is, in this case, a Cumulative Distribution Function (CDF), normalized according to its maximum value. It is referred to as  $F(t)$ . If  $\dot{m}$  is the mass or molar flow rate of tracer injected in a stream whose flow rate is  $\dot{v}$ , the peak concentration in the outlet stream is given by:

$$C_{max} = \dot{m} / \dot{v} \quad \text{Equation 24}$$

And the CDF normalized accordingly:

$$F(t) = C_{step} / C_{max} \quad \text{Equation 25}$$

The probability density function  $E(t)$ , and the CDF are linked by

$$E(t) = dF(t)/dt \quad \text{Equation 26}$$

The positive step input has just been described, but in practical experiments, it might be more convenient to use a negative step input. While adopting this procedure, the investigated system is continuously fed with a known amount of tracer, until the concentration of the tracer at the exit (at the measurement location) reaches its steady-state value. At  $t = 0$ , the concentration of the tracer in the inlet stream is suddenly stopped to its final value and kept constant indefinitely.

As the RTD is the response of a system to a known disturbance, the distribution of residence times for the ideal systems introduced in section 2.1 can be analytically retrieved [41]. To this aim, the concept of transfer function is applied. A transfer function is a function that models the output of a system for each possible input. The mathematical model of systems with regards to the investigated quantity must be written to obtain the transfer function.

Considering a CSTR, where  $\dot{v}_{in}$  and  $\dot{v}_{out}$  are the incoming and exiting flow rates in  $m^3/s$ , and  $C_{in}$  and  $C_{out}$  the inlet and outlet tracer concentration, the mass balance on the tracer concentration in a reactor whose volume is  $V$ , is written as follows:

$$V \frac{dC_{out}}{dt} = \dot{v}_{in} C_{in} - \dot{v}_{out} C_{out} \quad \text{Equation 27}$$

Transforming the previous balance equation to solve it in the Laplace domain (variable  $s$ ), and solving for  $C_{out}$ , one obtains:

$$C_{out} = \frac{(\dot{v}_{in}/\dot{v}_{out})}{\left((V/\dot{v}_{out})s + 1\right)} C_{in} = \frac{(K_P)}{(\tau s + 1)} C_{in} \quad \text{Equation 28}$$

Equation 28 is a specific case of the more general Equation 29, describing the evolution of a linear system:

$$\frac{\text{Output}}{\text{Input}} = G(s) \quad \text{Equation 29}$$

$G(s)$  is the transfer function of a generic system.  $K_P$  is referred to as the Gain, and  $\tau$  is the Time Constant [41] of the transfer function of the CSTR:  $G(s) = \frac{(K_P)}{(\tau s + 1)}$ . Using the transfer function, it is possible to retrieve the effect of variations of  $C_{in}$  on  $C_{out}$ . The analytical form of the RTD of a stirred reactor is obtained by returning into the time domain. For an isothermal system:

$$E(t) = e^{-t/\tau} / \tau \quad \text{Equation 30}$$

For a PFR, the discussion is even easier. According to the basic hypothesis behind the PFR, there is no back mixing of products and piston flow is ensured. Therefore, the exit of the system shows the same behavior as the entrance but delayed. The delay time between the injection of the tracer and its appearance in the outlet concentration is the physical time the flow takes to reach the outlet,  $\tau$ . Therefore, for a PFR:

$$E(t) = \delta(t - \tau) \quad \text{Equation 31}$$

The  $E(t)$  obtained for the two systems is shown in Figure 6. It is to be noted that, differently from the characteristic equations Equation 11-Equation 18, written for ideal flow reactors in the previous paragraph, the equations needed to describe the tracer evolution inside the system are time-dependent. RTD analysis studies the response of steady-state systems to non-steady disturbances and check whether new steady states are reached and how.

The analytical expressions for the RTD of the ideal flow reactors are the starting point to approach the analysis of real systems, characterized by more complicated RTDs. When dealing with such complex mixing patterns, simple flow models comprising a given number of tuning parameters can be fit to the RTD to understand the behaviour of the system under investigation, retrieve the impact of different operating conditions on the chosen parameters and estimate the performance of the reactor. These flow models are sorted as follows:

- one-parameter models,
- multi-parameters models.

The one-parameter models category comprises two main approaches to RTD modelling, briefly presented in the following.

- The dispersion model. This strategy superimposes a certain amount of dispersion [42] to the plug flow of a generic stream: in this way, it is possible to explain the peak broadening that follows the sharp injection of a tracer in a flowing fluid via a pulse-like input function. The dispersion parameter  $D$  is therefore the parameter that accounts for the non-idealities of the system considered.
- The tanks-in-series model. In this case, the treatment stems from the basic statement that a PFR can be regarded as an infinite number of CSTRs (referred to as “tanks”) in series. Being the CSTR model able to describe two opposite flow behaviours, a suitable number of CSTRs in series between 0 and infinite can reasonably describe the mixing properties of a general system. The tuning parameter, in this case, is the number of tanks to put in series.

One-parameter models are practical, flexible and applicable to a wide range of situations. However, they provide a one-dimensional description of the flow, making it not possible to account for large scale non-ideal flow phenomena, like recirculation or bypassing.

For a more elaborate modelling, multi-parameters models are applied. In these models, the ideal systems introduced in 2.1 act as basic construction blocks to setup a network of interconnected ideal flow reactors whose dynamic behaviour is as close as possible to the one of the investigated real configurations. In other words, the RTD that characterizes a non-ideal case is regarded as the response of a system consisting of ideal flow reactors arranged in a proper way, assuming the superposition principle. Therefore, the real reactor under investigation is assumed as the combination of ideal reactors arranged in a suitable way, whose mathematical description is well-known. This approach is exemplified in Figure 6.

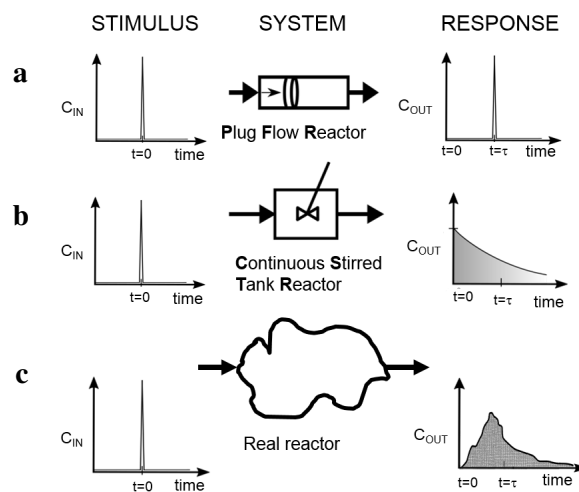


Figure 6: pulse responses of ideal system and generic response of a real system. **a:** PFR; **b:** CSTR; **c:** exemplified real reactor.

In other words, these models exploit the two simple ideal flow reactors introduced in paragraph 2.1, which represent the two extremes of the mixing possibilities. Any kind of complex flow relevant for

industrial purposes shows a behaviour that falls in between these ends and can be schematized by a combination of these, interconnected in a suitable arrangement. Such schematization is particularly advantageous because allows a basic understanding of the underlying phenomena behind a process. Furthermore, a simple model of a complex system is employed to carry out sensitivity analysis, study of troubleshooting and evaluation of reactor performance, enabling the improvement of said process and aiding the design of new ones.

These multi-parameters models are referred to as Compartmental Models (CM) or Chemical Reactor Network (CRN) models. Once an arrangement is designed, it needs to be properly sized by fitting the mathematical RTD of the model to the RTD measured in the actual configuration under investigation. This methodology is explained in the next chapter.

### 2.2.1 Chemicals Reactors Network fit

The problem that drives the present work, and more generally, the setup of suitable CM to reproduce the RTD of a system, can be stated as follows: given a Residence Time Distribution from a generic system, determine a Chemical Reactor Network whose RTD is the closest possible to the measured one. Generally, to design a CRN of a given configuration, the guidelines set by [43]–[45] are applied. In short, the listed steps are followed:

1. Establish the reactor unit representation. In this work, the reactors employed as base unit of the network are the ones introduced in paragraph 2.1: the CSTR and the PFR.
2. Design the arrangement of the network of interconnected reactors. The arrangement itself is also referred to as network superstructure: a superstructure is postulated that considers different feeding, recycling, etc., strategies for the reactor units. In this step, a network arrangement is designed, and it should include all the flow features that might occur in the process under investigation. These features comprise, as an example, recycling of part of the flow, or trapping of flow in dead zones. The chosen superstructures used in this work, and the criteria behind them, are explained in the following sections, 3.3.1 and 3.3.2, 4.2.1 and 4.2.2.
3. The designed superstructure is formulated as an optimization problem.
4. The optimization problem is solved.

More details are provided about 3 and 4.

Once a CM layout is designed, the values of several network parameters, or network variables, must be determined. These parameters are, usually:

- zones volumes,
- flow rates exchanged among the identified zones,
- temperatures or heat exchange coefficients if non-isothermal processes are considered.

For the mathematical treatment of the problem, the introduction of the tracer in a steady-state system is regarded as a disturbance of the system state. From a phenomenological point of view, it is necessary to describe the propagation of a generic disturbance, introduced with a generic input function, in a system [41]. The problem is therefore approached assuming a linear lumped-parameter system, a good approximation for single input-single output cases (SISO): it is defined by ordinary differential equations, describing the evolution of the concentration of the tracer in the network over time. Spatial gradients are not considered. In this scenario, a first-order linear system accounts for the CSTR, as in Equation 28, and a delay time accounts for the PFR, Equation 31.

A mathematical model is written for each base unit of the network, considering interconnections and flow splitting. It provides the equations to calculate the space-time of the adopted reactors ( $\tau$ ), and the gain parameters ( $Kp$ ) for the mixing of multiple streams, starting from the zone volumes and exchanged flow rate. For the generic reactor unit, the following equations are written:

Mass balance

$$\dot{m}_{in} = \dot{m}_{out}$$

Equation 32

Space-time calculation

$$\tau = V / \left( \frac{\dot{m}_{out}}{\rho_{out}} \right)$$

Equation 33

Where

$\dot{m}_{in}$	Incoming mass flow rate, kg/s	$V$	Reactor volume, $m^3$
$\dot{m}_{out}$	Outgoing mass flow, kg/s		
$\rho_{out}$	Density of the stream leaving the reactor, kg/ $m^3$		

Beside the reactors, other components constitute the network: splitters and mixers. A splitter allows a generic stream to feed more than one unit, as long as the mass balance is respected. It is characterized by the splitting ratio  $\alpha$ , that quantifies the ratio of splitter feed stream in all the splitter exit streams. On the other hand, a mixer merges two feed streams, coming from different reactors, and usually with a different tracer concentration. Their treatment is exemplified in Figure 7 and Figure 8.

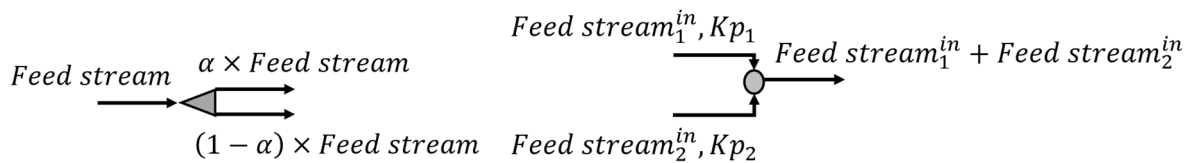


Figure 7: schematization of a splitting element.

Figure 8: schematization of a mixing element.

Equation 32 must be fulfilled in both cases. The evolution of the concentration of a generic species, in this case the one of the inert tracer that has been introduced, is treated as follows:

- Splitter: the concentration of the outgoing streams equals the one of the stream entering the splitter.
- Mixers: the equations are written following Equation 27, Equation 28 and Equation 29, and the  $K_P$  coefficients for each stream are retrieved.

The equations above are written for every component of the network: for each reactor, mixer and splitter, constituting the mathematical model of the system. This set of equations constitutes the mathematical model of the CRN. This model is implemented in Matlab® to allow for the calculation of the  $\tau$  and  $K_P$ . It is linked to a Matlab Simulink® flow chart that calculates the dynamic response of a given system: the network superstructure is reproduced in the Simulink® environment. In this environment, the dynamic response is calculated by stimulating the system with an input signal that acts as “disturbance signal”. It is propagated through the system, according to the dynamic behaviour of the base units and their arrangement. In the following chapters, the input function fed to the Simulink® model is the inlet signal measured during the RTD experiments. The Simulink® model comprises several components:

- the base units: either a first-order transfer function (CSTR) or a delay time (PFR)
- splitters: a stream exiting a certain zone can be distributed to more than one subsequent zone
- mixers: if more than one feed stream enters a reactor, the streams are assumed to perfectly mix in advance
- source components: source of a signal, usually the inputs to a model
- sink components: to collect and export signals, usually the outputs of a model

The output of the simulation is a curve over time (the RTD in this case) describing the dynamic response of the system to the disturbance introduced and is a function of the parameters identified for a given network in terms of volumes and flow splits. This curve is then compared to the experimental curve in terms of sum of the squared residuals: this is the objective function that must be minimized in order to retrieve the value of the network variables. To this aim the mathematical model coupled with the Simulink® flow chart is implemented in an optimization routine. The basic steps of the CRN-fitting routine are clarified in Figure 9. The Matlab Global Optimization Toolbox® and its built-in functions are employed.

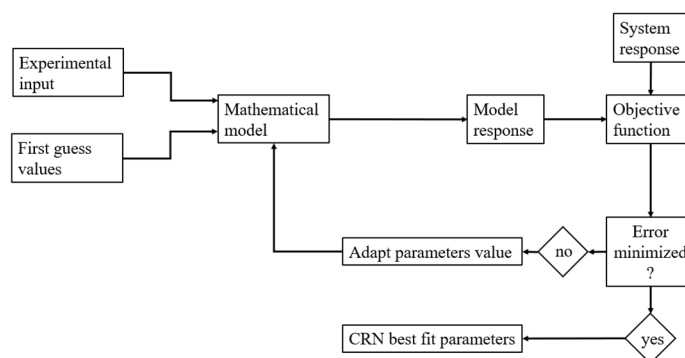


Figure 9: CRN-fitting procedure.

### 2.2.2 Chemical Reactor Network solver

Once the network has been calibrated against the RTD of the system, the chemical kinetics inside each reactor unit is solved by using a newly developed solver for CRN kinetic evaluation: NetSMOKE [46], a C++ code to solve reactor network models. An input file is written, comprising all the units, reactors and mixing/splitting devices, and is read by the program, that applies the required kinetic mechanism. All kinetic mechanisms can be used together with this solver.

## 2.3 Residence Time Distribution and Chemical Reactor Network

In the previous paragraph, the basics of RTD theory have been presented, and the importance of such quantity clarified. The response of a system to a stimulation with a known disturbance gives macroscopic information about the fluid dynamic behavior of the system itself. RTD data can be exploited in several different ways, each one crucial for the understanding of the facility under investigation.

As explained earlier, combustion in practical situations is a highly complex phenomenon: the transformation of the fuel often takes place in a highly turbulent environment, with peculiar features generated by the existence of a swirling flow, 1.2. Therefore, for a good understanding of the processes involved, description of both mixing and chemical reactions is needed. One way to deal with such a complex task is to start from the global response of the combustor, regarded as a generic system. This strategy approaches the complexity stemming from the intimate connection between mixing and chemical reaction from a macroscopic point of view. A direct exploitation of the RTD lies in the calculation of the main RTD moments, Equation 21, Equation 22 and Equation 23, from the distribution curve: in this way the overall mixing behaviour of the system is quantified by the calculation of few crucial quantities. Moreover, a complex reacting system can be modelled based on RTD data. This option is widely used, as it allows the comparison between ideal responses and the real response at hand by involving one or more parameters, that encase all the sources of non-ideality that apply to real systems. These models, called Chemical Reactor Network (CRN) models, or Compartmental Models (CM). They combine a good schematization of the mixing features with a detailed description of the chemical kinetics, meeting the necessary requirements to achieve an improved understanding of the process at hand. RTD-derived CRNs involve usually few zones, exemplifying the macro mixing features of a process. This coarse description encases also the strength of this modelling strategies: a low number of zones describing the gross flow structures allows the identification of the main mixing and reacting properties of the flow, enabling trend identification and guiding reactor design [35], [47], [48].

The works [37], [38] are among the first studies to lay the foundation of RTD notion. RTD theory is addressed from a mathematical point of view, linking it to the ideal flow reactors and deducing the analytical RTD for ideal systems. The author of [36] extends these works, adding further suggestion on the use of RTD. The field is further explored in [49], dealing with the connection between RTD and

micro mixing, while [50] summarizes the analytical ways to interpret the distribution of residence times in a system. Following these pioneering studies, RTD data have been used, and are still widely employed in the chemical industry, for design and troubleshooting purposes. More important, these data are actively used to gain insight on the effect of design variables on the performance of the system under investigation [51]–[53]. A review is provided about RTD in the industrial area, although limited to the use of radiotracers [54]. In general, these CRNs are rather simple and designed considering the features that are most likely relevant to the process. Therefore, although information about the output are obtained with this technique, a general compartment model does not make it possible to relate its base units to defined zones inside the reactor as pointed out in [50]. In combustion research, a good description of the mixing pattern is crucial. Therefore, the interpretation of RTD data is given in terms of main flow structures inside the system, as proposed by [47], [55]: in these works, it is already proposed to choose and connect the base units retrieving a correspondence between the ideal flow reactors and the flow features in the different zones inside the combustor. According to this strategy, the identification of zones with a preferred mixing pattern based on the local flow characteristics and their subsequent representation by means of a base unit is referred to as “zonal modelling”. A CSTR is used to describe a volume that has been identified inside a system if no preferential flow direction is present, whereas a PFR is preferred when a preferential flow direction is identified, as stated in [56]. According to this strategy, [57] presents a simple schematization of a gas turbine combustor employing a CSTR to model the first part of their facility, also referred to as primary zone, where reactants and fuel are mixed and the flame is stabilized, and a PFR to model the final part. It was shown that this reactor arrangement was indeed the one yielding the best performance. After this sensitivity study, they measure RTD in a water model of a furnace, and in the real furnace under reactive conditions. The tests proved that a real combustion device can indeed be approximated with the series of ideal reactors mentioned above. It was also noted that a different swirl number yielded a different value of the ratio between the stirred part and the segregated part. It was furthermore proved that the results achieved in the cold prototype model and those achieved in the furnace showed a good agreement if the swirl number was kept the same for both cases. This kind of study was proposed again by [58]. Building on the previous work, the authors carried out RTD measurements at the outlet of a model gas turbine combustor, varying the inlet position. In their opinion, measuring the output tracer response between various locations within the combustor was crucial in order to overcome the risk of non-uniqueness of the arrangement of ideal reactors in a network. The aim of the experiment was twofold, as it was carried out also to validate an algorithm to calculate the distribution of residence times starting from CFD data. The volume obtained for the primary, stirred zone in the combustor was used to determine the lean blowout limit for the investigated combustor. RTD data enabled the estimation of the primary combustion zone volume also in [59], where the tracer response with and without combustion was compared and commented in terms of entrainment of the tracer and frequency of the tracer peaks detected. [60], [61] faced the problem of the optimization of municipal waste incinerators. They dealt with it calculating the RTD from CFD results and analyzing it in terms of desired macromixing inside the system. Because of these studies, [60], [61], modifications for the improvement of the system were proposed, proving once again the relevance of the distribution of residence time for system design and optimization. The studies also highlighted that the geometry of the system itself plays a crucial role in the mixing process. The latter finding was supported by CFD and subsequent RTD calculation of the chamber with a modified geometry, that enhanced the mixing in the system under investigation. [62] carried out a similar work, developing their model based on the RTD obtained from CFD data of two pulverized coal flames furnaces. They proposed three simple CRN models of interconnected reactors based on the knowledge of main flow and mixing zones. The models were tested against the CFD-calculated tracer response for both ovens, which had different thermal output. These models presented few optimization parameters, obtained via optimization of the network response to the distribution of residence times. The developed network was optimized against experimental data as well, proving capable of adapting to several practical situation, and was exploited



in a subsequent work [63]. Here, detailed kinetics is applied to the reactors model in order to gain knowledge on the combustion of pulverized coal in a confined swirling furnace.

[47] exploited the finding from [57] about the swirl number in a cold or reactive case to carry out a RTD analysis in a scaled down version of a furnace. This work presents RTD measurements in a cold swirling flow, focusing on the effects of the swirl number. The measurements were carried out at three different locations inside the system: at the exit of the chamber, both at the centerline and off-centerline, and inside the internal recirculation zone formed by the vortex breakdown of the swirling flow, on the centerline. Based on the results obtained from these three measurements locations, the flow features were reconstructed, and a CRN was accordingly designed. It allowed a deeper insight in the mixing characteristics of the system with respect to [57], because few network parameters were identified and optimized based on the RTD data. The extreme simplicity of the network [57], though correctly reproducing the effect of the different operating conditions on the gross schematization of the flow pattern, does not properly highlight the different routes the flow might take inside such a system. Real combustion devices exhibit complex flow patterns comprising zones with different mixing characteristics parallel to each other, and a simplified version of the flow should consider them. This is what the networks [47], [62] try to include in their works. Referring to the Figure 10, they identify the recirculation zones and a jet zone, and arrange networks that consider their presence. The proposed arrangement follows the basics of zonal modeling, which, with the aid of Figure 10, are better explained as follows:

- mainly, a recirculation zone is represented by a CSTR: in a recirculation zone there is no clear flow from one point to the another. No specific direction can be identified and associated to the flow characteristic in a recirculation zone. This feature is the one that ensures intense mixing in a recirculation zone, allowing to consider it as a perfectly mixed volume, hence a CSTR.
- A PFR is chosen when a preferential flow direction can be identified, for example pipe flow or post-flame flow in a sufficiently long combustion chamber. For this reason, jets and the shear regions between the recirculation zones are usually represented as plug flow systems.

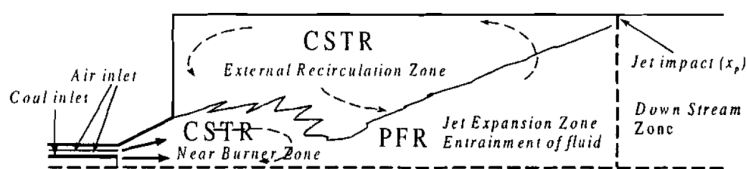


Figure 10: simplification of the fluid dynamics of a confined swirling flame, from [63].

The works [64], [65] acknowledge and exploit the power of RTD data for combustion chamber design purposes. More in detail, the authors measured the distribution of residence times in a secondary combustion chamber of a rotary kiln, together with temperature profiles. The flow pattern of the experimental facility had been investigated during previous measurements. The analysis of RTD and temperature data, coupled with the knowledge of the fluid dynamics of the system, aided the design of a network of interconnected flow reactors able to reproduce the response of the system. The simplified system highlighted issues in the mixing process, and modification of the system were proposed. Detailed kinetics is applied to the network of reactors in [64]. The emission trends were correctly predicted, although the overall agreement with experimental data was poor. Nonetheless, the correct identification of the trends confirmed the validity of the identified network: it was then employed to identify the sensitivity of these trends to the parameters of the CRN model.

Further works exploiting residence time distribution data to deepen the understanding of phenomena in gas turbine model combustors are [66]–[68]. [66] measures RTD in a gas turbine combustor with the aim of testing different injector arrangements. The differences between an injector arrangement comprising a central jet and one without the central jet were highlighted and explained by means of the tracer decay curves. RTD measurement have been carried out in [67] as well, and the RTD analysis was complemented by the design of a CRN to explain the observed phenomena in a scaled model of a

combustor. This work is extended in [68], exploring reactive conditions and exploiting RTD-modeling to assess the effect on the flow field of steam diluted conditions. Here lies the strength of such an analysis: when investigating new combustion concepts, RTD-analysis is a powerful candidate for a first examination of the impact of the new operating conditions with respect to the benchmark combustion process. In [68], the different mixing characteristics among cold flow, as well as reactive flow at dry and steam diluted conditions are highlighted and discussed, once again by means of a CRN analysis. The network proposed is a very simple one, showing a jet zone, two recirculation zones (internal, IRZ, and external, ERZ) receiving flow from it and a segregated zone downstream of the jet. The jet zone, having high flow velocity and a preferential direction, was modeled as a PFR, whereas a CSTR for each zone represented the recirculated flow regions. The zones were established based on zonal modeling of the flow; therefore, the volumes of the zones were deduced from the available PIV measurements in the different situations investigated. What emerged from the study, was that the volumes that refer to the different zones are indeed different when the operating conditions change, pointing out the importance of the zones volumes determination. [69], [70] investigated oxyfuel combustion atmospheres for both gas and coal flames exploiting RTD measurements. The results of the measurements were linked to the different flow and reactive behavior while investigating oxyfuel combustion by analyzing the principal moments of the distributions. A simple CRN, similar to the one in [57], was fitted to the data. The aim of this simple CRN-fitting was twofold. The first was to obtain smooth distribution curves out of noisy ones, without applying severe signal-filtering of the data. From these smooth distributions, the principal moments (Equation 21-Equation 23) were retrieved. In this case, a CRN-fitting was also employed as a suitable RTD signal-postprocessing strategy. Beside this application of the CRN, it proved once again to be a valuable tool to understand the impact of the operating conditions on the mixing pattern by allowing the calculation of the ratio between the stirred and segregated region while moving from air-fed combustion environments to oxyfuel combustion, varying the ratio  $CO_2/O_2$ .

## 2.4 Other Chemical Reactor Network strategies

Given the complexity of practical combustion systems, the chance of a simple, yet effective, schematization of the process employing ideal flow reactors is attractive. CRN strategies independent from RTD data have been developed and applied over the years.

A network of interconnected ideal flow reactors was recognized as the best option to model combustion in a practical environment [71] against the turbulent flame speed models and the microvolume burning models. What makes this analytical modelling appealing is that in each reactor a detailed kinetic mechanism is applied to model the combustion reaction. Furthermore, choose and connect the base units retrieving a correspondence between the ideal flow reactors and the flow features in the different zones inside the combustor aids the identification of underlying process. The authors of [55], [71], [72] identified the critical features and the corresponding zones in a combustion chamber in terms of mixing characteristics and modeled them accordingly using ideal flow reactors. The flow splits were grossly established based on the subdivision of the quantity of air required for reaction and available for secondary inlet and were refined using a program for flow pattern prediction and the available experimental data. The inclusion of the principal characteristics of the flow field in the model had the aim of enabling the investigation of flame stability characteristics as well, i.e. blow off. The model was used in the first place to get performance and emission trends and showed a good prediction capability in a later work [72], where the results were compared to experiments. In the latter work, the usage and strengths of a CRN are emphasized and framed referring to the need of emission reduction and new technology development. [73] designs a CRN to be employed as a hybrid combustion design strategy. It is based on turbulent mixing concepts applied to partially stirred reactors, which takes as its starting point the geometrical shape for a given design and predicts the performance variables (like blow-off, combustion efficiency etc.). The primary zone, in which combustion starts and occurs in a recirculation zone, where combustion products are recirculated to the root of the flame and stabilize it, was described

using two parallel CSTRs in a recycle loop. This strategy had been first adopted by [74], where this arrangement was employed to explore flame sensitivities while changing operation parameters. These first works state the extreme importance of being able to predict stability issues, crucial for gas turbine operation. The possibility of gaining blowout information from this zonal modelling of the combustor makes it appealing while in the designing stage. Several studies have been published with the precise aim of exploiting a simplified version of a combustor as a simple tool to gain stability information [32], [75]–[78]. In [32], [75] blowout conditions are investigated first using one CSTR to represent the primary combustion zones, and then retrieving a more complex network from CFD calculation, postprocessing the numerical results using a supra-grid approach that took into account several characteristics of the different zones. [76] used the same approach to achieve the reactors network, and applied it to vitiated combustion, proving the suitability of the CRN modelling to aid the study, design and development of novel combustion processes.

The usage of a reactors network to predict stability, and therefore the chance to gain information inside the combustor and not only at the exhaust suggest another strength of this tool: the possibility to estimate species formation and combustion performance in the different zones inside the combustor itself, though a really gross network (i.e., two or three reactors as in [57]) proved insufficient to this aim, as pointed out by [47]. Based on this consideration [79] put effort in designing a reactors schematization to include air staging and entrainment of flow in the near wall region. Based on their results from the model, they propose empirical correlations to predict pollutant formation in the different zones of a generic combustor. Following this path, the capability of the CRN modelling was successfully applied by [80], whose authors summarize the findings from previous works to design effective CRNs to include in a global plant simulation code. They strongly state the necessity of being able to describe the different combustion modes that take place in a combustion chamber, namely premixed or diffusive. These different possibilities of combustion operation pose the necessity of being able to consider diffusive processes while employing ideal reactors, that expect instead a homogenous mixture. To this aim, they rely on previous works [79], [81] and move from them to propose two different networks applicable to premixed and diffusive combustion. In this way, a premixed combustion and a Rich-Quench-Lean combustor are modeled. The works [82]–[84] deal as well with the representation of a diffusive combustion chamber, starting from the calculated fluid dynamic solution. The diffusion process is modeled using parallel reactors, and their operating network parameters are determined by the calculated mixture fraction.

The authors of [85] take advantage of a reactor approach to investigate the importance of the nitrous oxide pathway in lean premixed gas turbine combustion. They follow the example of [57] and prefer to use a simple series of CSTR followed by a PFR to represent the system. This model is then used to assess the influence of a different ratio between the volumes of the two reactors. The simplicity employed allows the authors to retrieve conclusions about the ratio that would decrease  $\text{NO}_x$  formation. This work represents the starting point for [86], [87] where the model was applied, respectively, to a lab scale GT combustor to identify the main mechanisms of  $\text{NO}_x$  and CO formation while changing the inlet parameters, and to investigate the role of unmixedness on the formation of those same pollutants in an industrial lean-premixed gas turbine engine combustor. In both cases, the CRN strategy gave insights into the main mechanisms responsible for pollutant formation in lean premixed operation. Further investigations about lean premixed operation for gas turbines are carried out by [88], [89], which retrieve a network based on the different zones that are identified in a combustor from both flow pattern and temperatures gained from CFD. In [89], and more in details in [88], the identified zones were located and explained on a phenomenological basis, and their volumes and the interconnections determined by the numerical results. The modelling approach was applied to several gas turbine applications, showing that the method had the ability to accurately predict  $\text{NO}_x$  and CO emissions for lean premixed gas turbine combustion applications.

As proved in numerous works ([32], [75]–[78], [82]–[84] and [88], [89]), the availability of CFD simulations of the investigated device is crucial because it aids the design of a proper CRN. Differently

from [60]–[62], where CFD results have been employed to calculate the RTD of a given configuration in order to fit a network of reactors, it is shown that the results from a numerical simulation can be directly exploited to achieve an intelligently designed CRN. This possibility results appealing because it couples CFD and detailed kinetics, overcoming the unfeasibility of the application of detailed mechanisms to numerical modeling. According to this strategy, the results of a generic numerical simulation are then the first step toward a CRN. An automated hybrid approach where a network is retrieved as a next step after numerical modelling is proposed [5], [27], where a network of interconnected ideal flow reactors represented an industrial boiler taking as starting point its calculated flow field. To achieve this result, each grid cell was regarded as an isothermal stirred flow reactor, and therefore the number of interconnected reactors matched the amount of grid cell generated for the flow field calculation. It is therefore clear that a huge number of reactors is achieved in this case. Clustering of the reactors-cells can be done starting from the CFD-retrieved network, to enable the analysis of the behavior of the combustor in terms of main macro zones. This approach have been often referred to, in the technical literature, as “hybrid CFD-CRN approach”. Turbulent temperature fluctuations were afterwards taken into account with the development of a Kinetic Post-Processor (KPP) [90]. The code was further improved in a successive work [92], which proposed a fully coupled and parallel algorithm. The improvements concerned the performance of the code, made more flexible and efficient using external libraries and distributing data and tasks among several processors.

The idea behind this hybrid approach, that retrieves a CRN directly from CFD results, is that a validated numerical simulation run with a reduced kinetic model contains all the relevant information, namely flow field, temperature and main species. Minor species like nitric oxides and carbon monoxide, which are the most harmful and therefore regulated and thoroughly investigated pollutants, need a detailed kinetic approach. Numerous research groups have so far followed this idea, achieving a CRN analysis of the system as a subsequent step of numerical simulations. These networks are attained either by the user, based on some criteria (i.e. temperature field/flow pattern) or can be automated. In the latter case, the number of interconnected reactors might be huge, differently from the former case, where a user retrieves a network based on observation of the calculated flow field. As a huge improvement with respect to [80], the same research group continued the work on the development and optimization of the hybrid modelling approach, developing their own CFD-CRN algorithm [93], [94]. These works propose innovative ways to deal with heat exchange as well: in [52] the thermal fluxes coming from radiation were included in the network construction via a correlative 1-D approach; in [53], the diffusive turbulent flux was also incorporated in the reactors equations, to correctly model the interaction between the idealized reactor zone and its surroundings. The CRN is inferred via a two-step approach, which considers first the flow pattern, and then refines the network considering the chemical condition of the identified reactors. [95] extract the network features from their CFD calculation using a fluid tracer and referring to the fluid age. The addressed quantity refers to the time the fluid has been in the domain and is exploited when determining recirculation flows. This methodology uses to a certain level the link between the Residence Time Distribution of the system and the network of reactors.

Though the proven effectiveness of an automated CFD-CRN approach, simpler approaches ([34], [96]–[98]) are preferred while investigating industrial applications and practical systems. The preference has several reasons. Among others, the possibility to relate a specific reactor to a region inside a combustor and understanding how the behavior associated with that zone changes while exploring a range of operating conditions. This aspect is particularly relevant, making a simple CRN the preferred tool for combustors design [34], [97]. In particular, [34] enlightens on the importance of the reactors network strategy, that is indeed incorporated into the design strategy of gas turbines combustors. The work shows that a network is obtained from the combined experimental and numerical investigation of a small-scale combustor, using the Siemens in-house 1D reactor network code. The zonal decomposition of the simplified combustor serves as starting point to design a simple reactor network of a full-scale combustor, the SGT-400. It is of course a complex configuration, as it features the introduction of cooling air along the combustor wall, and a more sophisticated model is required. This model, though

more complex than the previous one, keeps a small number of base units, easily relatable to different regions inside the system. [97] has the double aim to investigate LBO and NO<sub>x</sub> formation for H<sub>2</sub> enriched fuels. Both experimental and numerical investigations, which were previously carried out on the combustor under study, support the setup of a 4-elements CRN. The authors strongly state the necessity of such a simple and flexible tool to aid the design and optimization of combustion-based devices. Understanding NO<sub>x</sub> formation under gas turbine-relevant conditions concerns as well the works [98]–[100]. The network parameters are derived from CFD simulations, and they compare a basic network, comprising 4 units, with a more elaborate one, including up to 17 units. Though the complexity of the model is increased, the zones are easily relatable to well defined regions inside the investigated combustor. The agreement between the model prediction and the experimental data was good already for the basic model, confirming that, despite its simplicity, it could capture the significant mixing and reaction characteristics. The increased complexity of the second model did not improve the prediction significantly.

As already showed in the initial part of this section, close-to-reality configurations are successfully modeled using a CRN also without the aid of CFD. According to previous works like [55], [71], [73], component modeling is often used to retrieve a network. This strategy relies on relationships applied in smaller control volumes and local phenomena (i.e., liquid fuel evaporation) identified inside the system. From these relationships the relevant information for the setup of a network of interconnected reactors is obtained, as shown in [101]. A specific review about hybrid emission modelling methods applied so far is given in the first part of [102]. These hybrid emission models are applied to gas turbines in [103]–[105], and to an industrial furnace in [106]. The authors [107]–[110] rely on zonal modeling of the flow to interconnect the base units. To size the network, optimization routines are employed, defining an objective function based on available emission and performance data. As a correct determination of the volumes of each reactor is crucial, both volumes and the flow rates of each zone are retrieved by the calibration of the network. Such technique has the advantage of being faster than a CFD-based one and to give insight into the macroscopic features controlling combustion phenomena.

An interesting suggestion on the unexplored potential and future use of the CRN modeling strategy comes from [111]–[113]. The purpose of these works to prevent lean blowout in gas turbines setting up an on-line CRN modeling, during combustor operation. To this aim, the network is kept simple, retaining the description of the main flow and flame zones, and boundary conditions (feed stream mass flows, inlet temperatures, etc.) are live taken from the monitoring system of the facility. In this case, the simplicity of the network was crucial to gain knowledge on the impact of the operating parameters on the identified macro-mixing zones. The proof-of-concepts of a Real-Time CRN was successfully demonstrated. The CRN monitored species and radical formation and proved a valuable control methodology to prevent incipient lean blowout.

## 2.5 Summary

Combustion in practical configurations is an extremely complex phenomenon: the transformation of the fuel takes place in a highly turbulent environment, with peculiar overall features generated, for example, by the existence of a swirling flow. Therefore, for a good overall understanding of the processes involved, a good description of both mixing and chemical reactions is crucial. The huge complexity of this task requires the development and use of simple and flexible analysis tools, whose aim is to give insight into the mechanisms of the process considering both fundamental aspects of practical combustion facilities, like furnaces and gas turbines.

Chemical Reactor Network (CRN) models, or Compartmental Models (CM), match the requirements set by the need for a description of the mixing features together with a detailed description of the chemical kinetics. In this chapter, the different strategies to achieve a CRN have been reviewed, together with the results achieved by the different research groups. A CRN is designed by applying different methodologies:

- regard the RTD as the transfer function of the system under investigation, and design and size the network to reproduce it
- fit the network of ideal reactors to know emission data or rely on fluid dynamic and design equations
- exploit CFD to retrieve the network. This process can be:
  - automated,
  - user defined.

This work focuses on Chemical Reactor Network modelling of two close-to-reality combustion configurations exploiting Residence Time Distribution data.

Choosing this methodology, experimental evidence is collected that yields important information about the mixing properties of a non-ideal flow and the impact of boundary conditions on its behaviour. This information is obtained before the application of the CRN modelling and does not depend on it. Furthermore, RTD-driven CRN are generally kept simple, allowing the identification of the fundamental mixing zones that characterize a system. This is once again important for sensitivity analysis, because it makes it possible to practically understand the effect of a changed boundary condition on the specific zone behaviour. In addition, validated CFD results are often not available, especially for extremely complex configurations that feature complex technological characteristics of real combustion facilities. In these cases, a tracer experiment allows the user to collect valuable information on the behaviour of the device.

Up to now, as shown in paragraph 2.3, RTD-driven CRN have been applied for various purposes, and the models were often critical in aiding the practical design of the investigated apparatuses. What has not yet been thoroughly addressed is the exploitation of RTD data to design a reactors model where detailed kinetics can be applied. Given the significance of RTD in characterizing a system, and the proven chance to reproduce the response of a system by means of a network of reactors, the possibility to extend RTD-driven CRN to investigate the reactive features of a configuration must be explored. In order to do so, the network should incorporate the critical flow characteristics, exhibiting a higher number of network units with respect to the extremely simple RTD-derived CRNs. Then, coupling RTD analysis and CRN solved with detailed kinetics, the practical design of combustion devices is guided considering both crucial aspects of mixing and chemical reaction.

Therefore, after the identification of this yet unexplored research possibility, the purpose of this work is to explore the capabilities of RTD-driven CRNs coupled with detailed kinetics. Such a modelling is applied to two close-to-reality configurations, gaining insight into the underline mixing and reacting processes.

### 3 Gas Turbine Model Combustor

The modelling strategy introduced earlier, section 2, is applied to a Single Sector Gas Turbine (SSGT) model combustor designed at Technische Universität Darmstadt, and presented in [18], [114]. RTD measurements have been carried out in this apparatus, with the aim of exploiting the data to design and size a network of ideal flow reactors able to reproduce the mixing and reactive characteristics of the experimental configuration. The model has then been used to gain knowledge on the effect of the operating conditions on the mixing and reactive features of gas turbine combustion.

In the following, the SSGT and the measurement setup for RTD data collection are presented. Afterwards, the CRN models are designed and fit to the data. A discussion on the results follows, for both non-reactive and reactive operating conditions.

#### 3.1 Experimental apparatus

The investigated apparatus is shown in Figure 11. It consists of a pressurized Single Sector Gas Turbine model combustor (SSGT). To create engine like boundary conditions, the test rig is housed in a pressurized vessel, shown in grey. The pressure of the system is increased and controlled by means of a throttle downstream of the outlet pipe of the combustion chamber, not shown in Figure 11. A deeper explanation is found in [18]. A movable block swirl generator (TECFLAM), shown in orange and in Figure 12, generates a swirl flow with central recirculation to stabilize the flame. This component allows changing the geometrical swirl number, ranging from 0 to 1.7, to generate flow patterns typical of technically relevant combustion systems. As explained in paragraph 1.2.2, the operating fuel is natural gas. It is fed either before the movable block, with the main air feed or directly into the combustion chamber via a central pilot jet. There is, therefore, the chance to investigate purely premixed as well as partially premixed flame, reaching also purely diffusion flames. For premixed operation, six inlet nozzles arranged radially around the main air plenum bring the fuel directly in the main air flow entering the swirler. For fuel-staged operation, the natural gas is additionally issued by the central pilot, yellow colour in Figure 11. A detail of the swirl generator, together with the bluff body/pilot tube, the main air intake and the fuel inlet nozzles for premixed operation is shown in Figure 12. A subsonic exit nozzle guides the flue gas outside the combustion chamber (red colour in Figure 11), where they are mixed with the pressure vessel cooling air. The right and left sides of the combustor are optically accessible over the whole size, whereas the upper side is in part optically accessible.

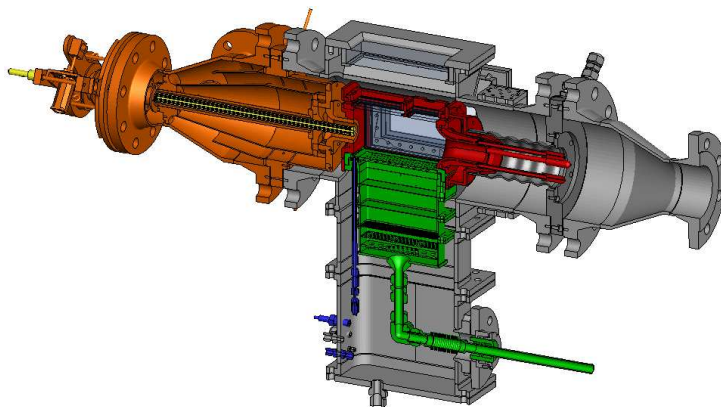


Figure 11: Main components of the SSGT test rig. Grey, pressure vessel; red; flame tube; orange, movable block radial swirler; blue, ignition torch; green; effusion cooling liner.

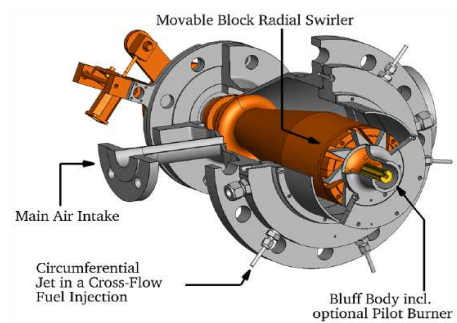


Figure 12: Detail of the movable block radial swirler and nozzles for fuel injection [18].

On the bottom side, there is an effusion-cooled wall (shown in green in Figure 11 and magnified in Figure 13), whose cooling geometry can be changed to study the effect of different cooling geometries

on the flow and reacting field. The presence of the effusion cooling liner is a crucial feature of this experimental apparatus, enabling the investigation the interaction between combustion and cooling air.

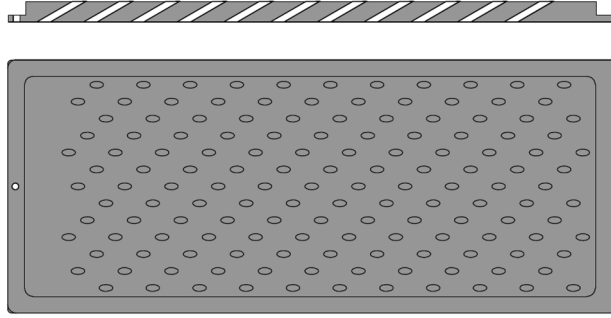


Figure 13: Top down and section view of the effusion cooling plate. Holes are inclined  $30^\circ$  with respect to the horizontal axis [18]. This effusion cooling plate features an ensemble of 145 holes.

A hot air wind tunnel feeds the effusion cooling liner, to ensure the homogeneity of the cooling air flow pattern inside the combustion chamber. Figure 11 shows in blue the  $H_2$  torch that is used in an initial stage, to ignite the reacting mixture. The current reference operation point, also referred to as “standard operation point”, is summarized in Table 1.

Table 1: Relevant parameters of the standard operation point and flame tube dimensions.

Operation point, units			Flame tube dimensions, m	
Preheating temperature	623	K	Height	0.1
System pressure, $P$	0.25	MPa	Width	0.1
Main air mass flow, $m_{in\_main}$	0.030	kg/s	Length	0.18
Equivalence ratio, $\phi_{lean\ premixed}$	0.75	[-]	Effusion cooling length	0.152
Swirl number, $S$	0.7	[-]	Hole diameter	0.002
Effusion cooling mass flow, $m_{cool}$	0.015	kg/s		
Thermal load	65.5	kW		
Reynolds number	25300	[-]		

All mass flow rates entering the combustion chamber, namely fuel, oxidizer and effusion cooling mass flow, are regulated by mass flow controllers (MFC, Bronkhorst).

### 3.2 Residence Time Distribution measurements

Residence Time Distribution measurements have been carried out in the SSGT. The aim of this experimental campaign was twofold: gain insight on the influence of the operating conditions on the global mean residence time and mixing pattern inside the combustion chamber and obtain the relevant parameters for to size a Chemical Reactor Network representative of the flow and mixing field inside the test facility.

The basic principle behind the measurements of RTD is simple: an inert tracer is injected in the system under investigation, its input function as close as possible to a dirac pulse, and its temporal outlet profile is monitored at the exit of the system. Its implementation is, however, far from trivial. Problems might arise from the flow non-idealities, the difficulties in injecting the tracer “close enough” to the entrance of the investigated reactor, and the choice of the detection strategy. In the following, a brief review of the strategies applied to deal with the task in close-to-reality combustion configurations is proposed.

Beèr and Lee, 1965, [57] measured RTD in strongly swirling flow, in a water model of a furnace, and in the real furnace under reactive conditions. Among the input function possibilities, the authors fed the tracer into the system using a negative step input function. This is the best choice if experimental issues prevent a pulse function [40], though this is stated because it was found that a negative step generated a



less noisy signal compared to a positive one. This was observed in [69]. However, [70] investigates this aspect further, and it was proven that a negative step induces a bigger error on the initial part of the signal, whereas a positive one has a worse effect on the final part, stating once again the importance of a well-implemented input strategy. The tracer used in [57] was a salt solution, probed by means of conductivity cells, in the cold prototype and Argon, detected by means of the chromatographic method, in the furnace. The authors of [58] carried out RTD measurements sampling the temporal profile of a tracer at the outlet of a model GT combustor, varying the inlet position. In their opinion, measuring the output tracer response between various locations within the combustor was crucial in order to overcome the risk of non-uniqueness of the arrangement of ideal reactors in a network. The measurements themselves were carried out using a method previously employed by the authors of [59]. In this work, a pulse of mercury vapor was injected into the test rig to determine the RTD of a flow past a V-gutter flame holder. The tracer was detected by measuring the absorption of radiation from a 254 nm mercury-neon hollow cathode lamp. Both works, [58] and [59], realized a pulse input function for tracer injection. RTD measurements in a scaled down version of a furnace were also carried out by [47]. This work presents RTD measurements in a cold swirling flow, focusing on the effects of the swirl number. Helium was fed into the combustion chamber with a negative step input function and detected by a fast response probe. Following the example set by [58], the point wise measurements were carried out at three different locations inside the system: at the exit of the chamber, both at the centerline and off-centerline, and inside the internal recirculation zone formed by the vortex breakdown of the swirling flow, on the centerline. A secondary combustion chamber of a rotary kiln is studied via RTD analysis in [65]. The tracer,  $\text{SO}_2$ , was step-fed and sampled to be analyzed in a gas analyzer. [115] explored the use of alkali atoms as tracer, to probe by means of Tunable Diode Laser Absorption Spectroscopy (TDLAS). Different injection strategies were proposed, and a pulse-like input was identified to yield the best results. [66] measured RTD via Planar Laser-Induced Fluorescence (PLIF) of a dye tracer in a water model of a gas turbine combustor. The dye was used to simulate the fuel flow. It was injected until it reached a steady state, and then rapidly cut off. Simultaneous PIV measurements were taken to ensure that the flow cut did not change the flow pattern inside the test facility. The mass flows were adjusted by matching the momentum flux ratio of a combustor flow. PLIF of a dye tracer in a water model was employed by [67], realizing a pulse-injection in a water model of a gas turbine combustor. This work is extended in [68], exploring reactive conditions, as well as steam diluted conditions. The measurement technique is different in this case, and the Quantitative Laser Sheet [116] (QLS) was instead applied. A step input was chosen because it was considered more robust with respect to the highly turbulent combustion environment. [69], [70] deal with RTD measurements by means of TDLAS. Cold- and reactive-flow measurements were carried out in a scaled down version of a furnace to investigate oxyfuel combustion [117], [118]. The tracer was methane for non-reactive conditions, and HCl for the reacting case. Several injection strategies were tested (positive and negative step, and pulse) and compared. As clarified before, the pulse input yielded the best results.

In the present work, to measure the distribution of residence times in the SSGT ([18], [114] and Figure 11), the Light Extinction Measurement (LEM) technique was employed. This technique uses a laser beam passing across a control volume, and the residual laser light after the control volume is measured. Laser-extinction diagnostics is suitable to follow the dynamics of fluids and embedded particles. It is therefore vastly employed for soot measurements ([119], [120]) as it provides spatially and temporally resolved measurements of attenuation from combustion-generated soot within the path of the beam. Optical extinction diagnostics rely on measurements of attenuation of a beam of light by a light-blocking medium. The attenuation of the probing beam is continuously monitored by dedicated equipment (photodiodes for example). The continuous monitoring of the light passing a certain control volume makes it suitable for time-resolved measurements and, more specifically, for non-stationary processes, like those involved during RTD measurements. Given the suitability of the LEM technique to capture transient processes and the flexibility of the required experimental setup, it has been adapted to measure the RTD of the gas turbine combustor. Soot measurements exploit the LEM method by correlating the

intensity of the incident light and the intensity of the light after passing a control volume exploiting the Lambert-Beer equation (see below, Equation 36 in paragraph 3.2.2). In such a way, the soot volume fraction is retrieved by calculating the optical density of the observed medium. To determine the RTD of a system it is necessary to record the transient evolution of the tracer concentration at specific locations. Therefore, it is not necessary to sample the intensity of the incident light, and the non-stationary extinction of the probing laser beam by means of a light-blocking tracer gives the desired quantity. Despite the differences between soot measurements and RTD measurements, as the methodology has been successfully applied in conjunction with solid particles, a solid tracer has been selected in this study: Alumina ( $\text{Al}_2\text{O}_3$ , diameter  $\sim 1 \mu\text{m}$ ) particles were chosen as process tracer. Furthermore, solid tracers applied to RTD measurements have been successfully applied in combustion environments while burning gaseous fuels [68].

### 3.2.1 Measurement setup

As mentioned in section 3.2, RTD was measured by means of the LEM technique, using Alumina ( $\text{Al}_2\text{O}_3$ , diameter  $\sim 1 \mu\text{m}$ ) particles as process tracer. The Stokes number,  $Stk$  in Equation 34, that measures the flow tracer fidelity, was calculated to ensure the suitability of the tracer.

$$Stk = \frac{t_0 u_0}{l_0} \quad \text{Equation 34}$$

$u_0$ : fluid velocity;

$l_0$ : characteristic length;

$t_0$ : relaxation time of the particle, Equation 35.

$$t_0 = \frac{d_p^2 \rho_p}{18 \mu_g} \quad \text{Equation 35}$$

$d_p$ : tracer particle diameter;

$\rho_p$ : particle density;

$\mu_g$ : viscosity of the fluid.

For  $Stk < 1$ , the particles fully follow the flow streamlines.  $Stk < 0.1$  is a threshold below which tracing accuracy errors are below 1%. In this work, the order of magnitude for  $Stk$  during non-reactive measurements is  $5 \times 10^{-4}$ . Particles are therefore assumed to properly follow the flow streamlines, and the RTD measured employing solid particles equals that of the gaseous flow.

The particles were fed to the system using a pulse input function. To achieve it, a flow bypass piece was designed and installed on one of the fuel inlets, Figure 14. While carrying out RTD measurements, the fuel flow was distributed among five inlet nozzles instead of six. Part of the main air flow ( $m_t$ , 0.002 kg/s out of 0.03 kg/s) was diverted to the bypass section and used to entrain the seeding in the combustion chamber. While the extinction signal was not recorded, the diverted air flow was flowing in the upper part of the bypass system, Figure 14. The  $\text{Al}_2\text{O}_3$  was batch-fed from the valve  $v_t$ , while  $v_2$  and  $v_3$  were closed to maintain the system pressurized. The valve  $v_f$  is a fast-switching valve (FESTO, switching time 2 ms) connected to a switch. After the tracer is fed, the valve  $v_t$  is closed, while  $v_2$  and  $v_3$  are opened again. The valve  $v_f$  is triggered by the switch and diverts the flow path of  $m_t$ , so that its passage in the lower path of the bypass system entrains the seeding to the combustion chamber. The experimental apparatus produces a pulse input, as is shown later. The switch triggers also the data acquisition program (sampling frequency 500 kHz, sampling time 1 s).

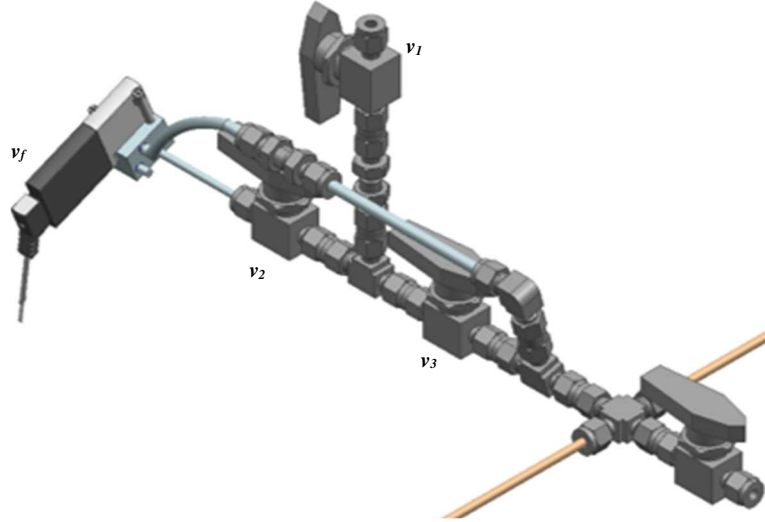


Figure 14: sketch of the bypass device. Unseeded flow  $m_i$  flows in the upper path,  $v_f$  switches the flow to the lower path to entrain the seeding for the measurements.

The light from a 1527 nm diode laser (Thorlabs) was used as probing light. The laser was connected to a 1:4 custom made fiber splitter, and the light was guided by means of laser fibers to four different detection positions, described in the following and shown in Figure 15 and Figure 16.

- 1: right after the entrainment of the tracer. The first extinction signal is collected outside the combustion chamber, in the bypass system. This is achieved by housing the laser fiber in a steel pipe, highlighted in orange in Figure 14 so that it fits in the cross connector. A lens is fixed at the end of the first part of the pipe, to focus the laser light on a photodiode (extended InGas, Hamamatsu), which is fixed on the other half of the pipe. The aim of this measurement is to collect the extinction profile as close as possible to the seeding-collection location.
- 2: at the entrance of the combustion chamber. Here, a line lens apparatus (Thorlabs) generates a laser sheet to collect the extinction signal over part of the inlet annulus cross-section. The light is focused on a photodiode by means of a spherical lens (Thorlabs). Before the photodiode, a 1530 nm filter (Thorlabs) blocks the light emitted from the flame in the detection range of the photodiode.
- 3, 4: at the exit of the combustion chamber. Here, the signal is simultaneously recorded in two positions: one at the centerline (referred to as  $Out_1$ ) and one  $\sim 10$  mm below the centerline (referred to as  $Out_2$ ). The aim of the latter probing position is to check for any non-uniformity of the exit tracer concentration along the cross-section as a consequence of the cooling air, issuing from the lower side of the combustion chamber. The laser fibers are equipped with GRIN lenses. The light is directed on the recording photodiodes by means of gold coated  $90^\circ$  off-axis parabolic mirrors (Thorlabs). Undesired light from flame luminosity is filtered as for the previous case.

The photodiodes are linked to current-to-voltage converters (Femto), which are connected to a four-channel oscilloscope (Tektronix) for on-line monitoring. The signal is recorded to a personal computer with a DAQ acquisition system (National Instruments), triggered by the same switch that triggers the fast-switching valve,  $v_f$ .

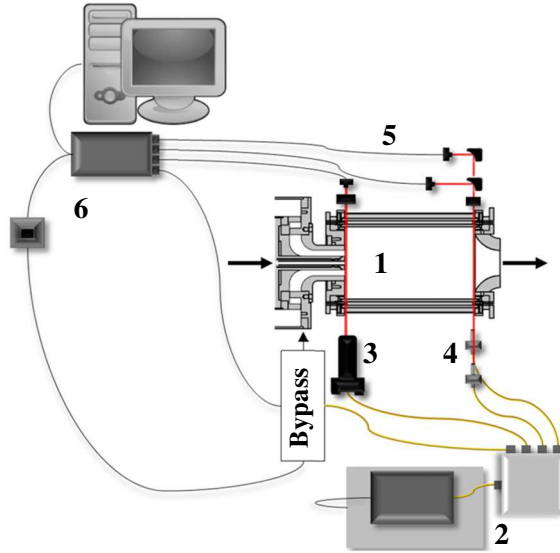


Figure 15: schematic of the measurement setup  
 1. Combustor and bypass system (more in Figure 14)  
 2. Laser apparatus, comprising a 1→4 fiber splitter to split the signal to the measurements channels  
 3. Line lens – entrance nozzle signal (Figure 16)  
 4. Laser beams – combustor exit (Figure 16)  
 5. Detection side photodiodes  
 6. Trigger switch and signal acquisition system

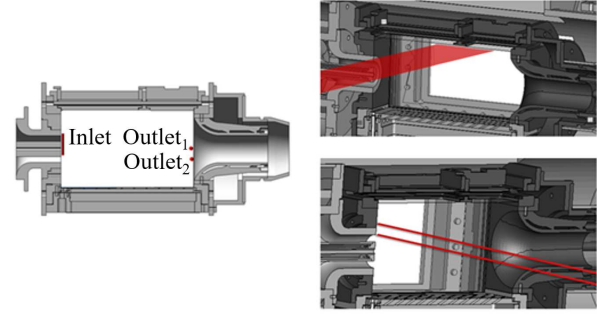


Figure 16: explanation of the measurements locations inside the combustion chamber.

A sketch of the measurement setup is proposed in Figure 15, where a schematic representation of all the main components is given. The black lines represent electrical connections, while the lines drawn in yellow represent the laser fibers issuing from the 1:4 fiber splitter. The bold black arrow indicates the direction of the flow of reactants entering the combustion chamber. Figure 16 shows a detail of the output probing points, not distinguishable from the perspective in Figure 15. As mentioned earlier, the feeding of the tracer is a batch operation. For each one of the explored operation points, the following steps, in the presented order, are followed:

1. Establishment of the desired operating condition and wait for the steady state to be reached.
2. While the bypass flow rate is flowing in the upper part of the bypass device, shown in Figure 14, close  $v_2$  and  $v_3$ , and feed the tracer through  $v_1$ .
3. Close  $v_1$  and open  $v_2$  and  $v_3$ .
4. Use the trigger switch to change the flow path of  $m_t$ . In this way, the tracer fed during step 2 is entrained and transported to the combustion chamber. The extinction signal for all the channels is automatically recorded.
5. Repeat steps 2-4.

Due to the batch nature of the process, for each operating condition tested the tracer measurements were carried out 10 times, i.e., step 5. was repeated 9 times. The single-injection results are then averaged to obtain a single extinction signal representative of the investigated point of operation. The choice to measure each operating condition ten times is based on a signal-to-noise ( $S/N$ ) ratio analysis, shown in Figure 17: here, the variation of the signal-to-noise ratio with the number of injection used to compute the average signal is reported for the non-reactive (upper row) and reactive (lower row) case. Two different boundary conditions were considered:  $m_{cool} = 15 \text{ g/s}$  (corresponding to the set of boundary conditions identified as “standard operation point” in Table 1) and  $m_{cool} = 7.5 \text{ g/s}$ . All the images show that the ratio has reached a flat level, and further gain that might come from an increased number of measurements would not be crucial for the average signal. To prove this point, one set of measurement, corresponding to reactive  $m_{cool} = 15 \text{ g/s}$  (lower row, left), has been taken twice, and the effect of a higher number of tracer injections evaluated in terms of  $S/N$ : it is clear that the ratio does not bring a substantial improvement to the investigated parameter, and ten measurements was taken as the suitable number of measurements. The choice to refer to the specific boundary conditions reported in Figure 17 is linked to the availability of CO measurements for these operating conditions from a previous measurement campaign [121]: as these measurements are employed in the following paragraphs to assess the performance of the reactive CRN in terms of CO emissions, the same set of

boundary conditions has been taken as reference. For this reason, sensitivity analysis and error estimation presented in the following paragraphs are applied to these two situations, taken as benchmark both for non-reactive and reactive operation.

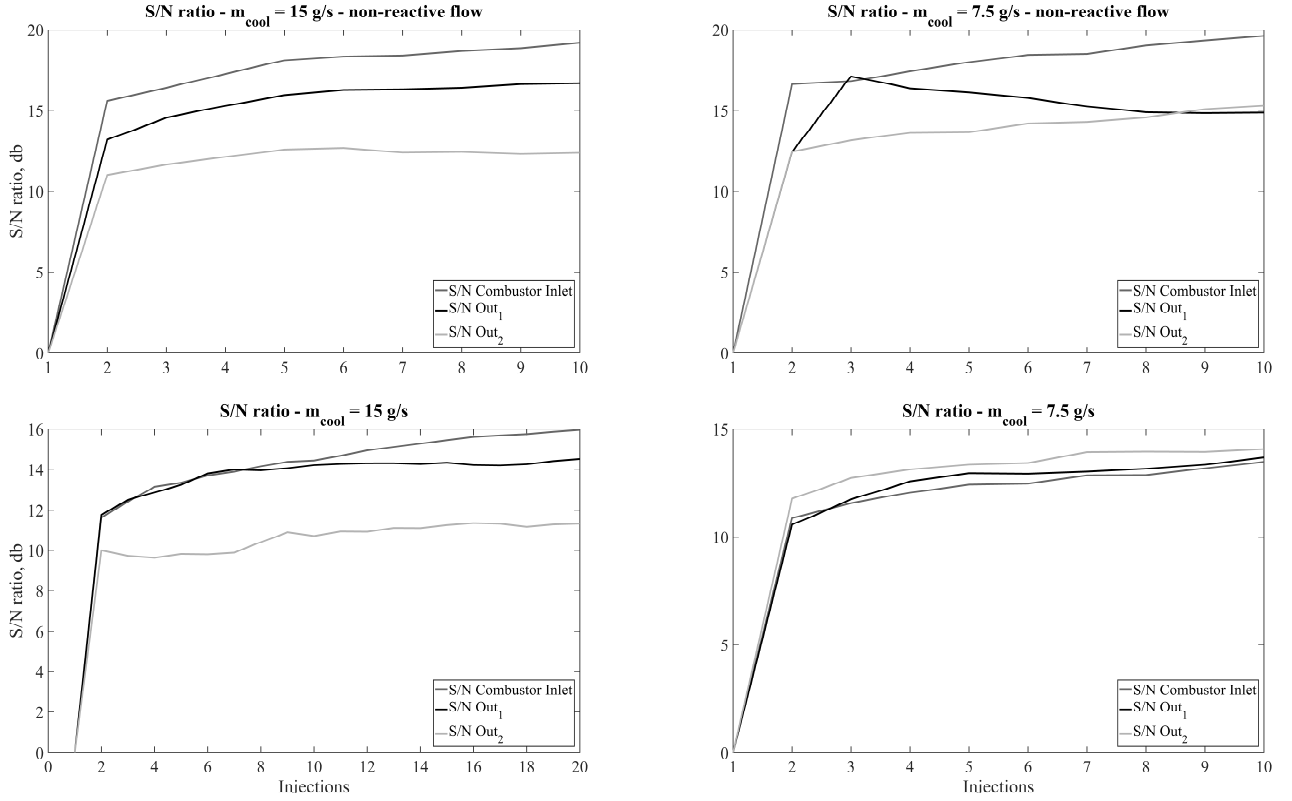


Figure 17: signal to noise ratio for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , non-reactive flow (upper row) and reactive flow (lower row). The Inlet Pulse has not been considered for S/N analysis.

The boundary conditions were varied according to Table 2, where the differences with respect to the reference point of operation are highlighted.

Table 2: explored operation points.

Parameters that are varied	Explored values, units	
Equivalence ratio - $\phi$	0.65, 0.75 and 0.85	[-]
Pressure - P	2.5 and 3	bar
Cooling mass flow - $m_{cool}$	15 and 7.5	g/s
Swirl number - S	0.7 and 1.3	[-]
Combustion mode – St.	0%, 10%, 30 % and 50% fuel staging	[-]

### 3.2.2 Experimental data treatment

In order to derive residence time distributions from raw data, several processing steps were implemented:

- Baseline correction. This step was necessary because of the progressing fouling of the optical windows, due to the deposition of the tracer. To this aim, an estimation of the start and end time of the extinction signal was required.

The start time was calculated as the time required for each channel to reach a threshold percentage of the maximum extinction value. The value of 2% was found to be suitable to properly catch the start of the signal. The end time was taken as four times the time corresponding to the maximum extinction reached. This estimation is based on a rule of thumb

proposed by [39], though concerning the adequate observation time and not the end time: it was proposed that the observation time should be taken as three or four times the mean residence time in the investigated system.

Once this information was obtained, the fouling was assumed to be a linear function of the sampling time, and therefore, the light intensity to decrease linearly to the final value. The extinction was then calculated using the Lambert-Beer equation:

$$E_l = \log_{10}(I/I_0) \quad \text{Equation 36}$$

$E_l$	Extinction, absorbance of the material for light with a wavelength $l = \lambda$ .
$I$	Intensity of transmitted light
$I_0$	Intensity of incident light

- Smoothing of the data using a moving average filter. To remove part of the background noise, the signals were filtered using a moving average filter, with a 400-points interrogation window. This simple smoothing has been applied in a similar situation [68] and proved sufficient to prepare the data to the subsequent fitting via CRN modelling.
- Area normalization. The resulting signals were normalized by their area to obtain the corresponding distributions. These results, although not strictly corresponding to the RTD of the investigated combustion chamber (see 3.3.1.3 and 3.3.2.2), are referred in the following as “ $E(t)$ ”.
- Averaging of the single-injection measurements.

An additional step was required for the inlet pulse signal, before the post-processing steps, in order to use the signal for the CRN modelling. As explained earlier, this signal was taken immediately after the entrainment of the tracer by the bypass air, namely the highest concentration of tracer in the system. This led to saturation of the light extinction signal, i.e. the extinction curve could not be captured completely but it was rather clipped before reaching the maximum of the distribution. As such a signal was not exploitable for further use without an additional step, the inlet pulse injection signals have been fitted by a curve comprising a sum of Gaussian curves before proceeding with the processing. The resulting curve was taken as the inlet pulse distribution.

The post-processed distributions for the four acquisition channels, after treatment and area normalization, are shown in Figure 18, non-reactive flow, and Figure 19, reactive flow. Behind each curve, the single-injection results are superimposed to each other, as an indication of the experimental variation. The standard deviation for the sample channel is also reported. For both reactive and non-reactive flow, two operating conditions are reported:  $m_{cool} = 15 \text{ g/s}$  (corresponding to the set of boundary conditions identified as “standard operation point” in Table 1) and  $m_{cool} = 7.5 \text{ g/s}$ .

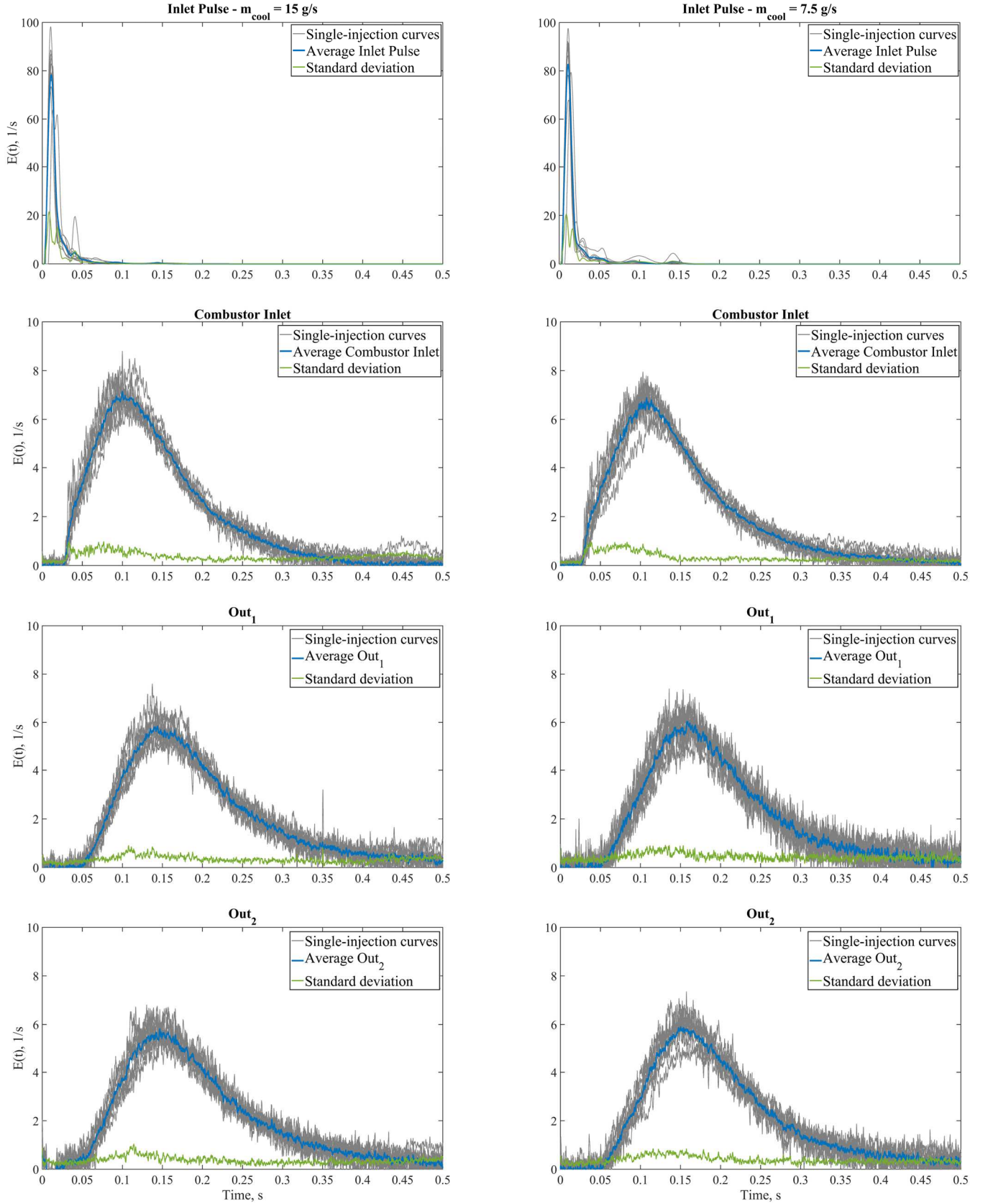


Figure 18: average RTD, superimposed to the single injection curves for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , non-reactive flow. The standard deviation is also reported.



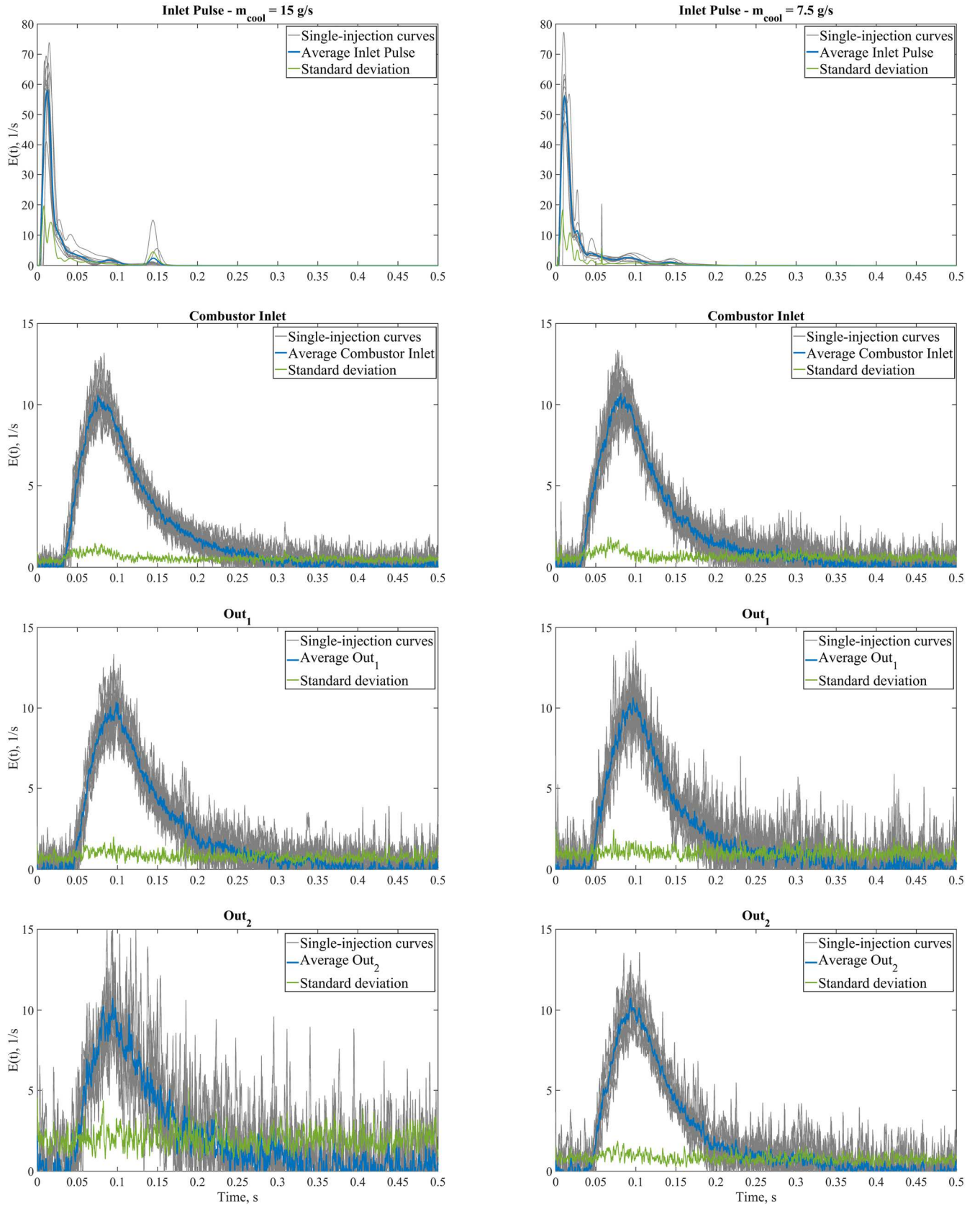


Figure 19: average RTD, superimposed to the single injection curves for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , reactive flow. The standard deviation is also reported.



### 3.2.3 Experimental results

Several operating conditions have been explored (listed in Table 2) and the tracer response for each condition collected. By comparing these responses to the standard operating point (relevant parameters listed in Table 1) the impact of the boundary conditions on the mixing properties of the system is retrieved. This comparison is carried out in a later section, paragraph 4.3. At this stage, the CRN both for non-reactive and reactive condition has been designed and optimized against the experimental curve, and the fitting results are used to carry out the comparison. Adopting this strategy, smoother curves are compared, enabling a clearer identification of the features that characterize a certain set of boundary conditions. Therefore, in the following, a comparison between pure experimental curves is only reported for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , for cold and reactive flow field. The mean residence time is also calculated from the experimental responses for the presented operating conditions.

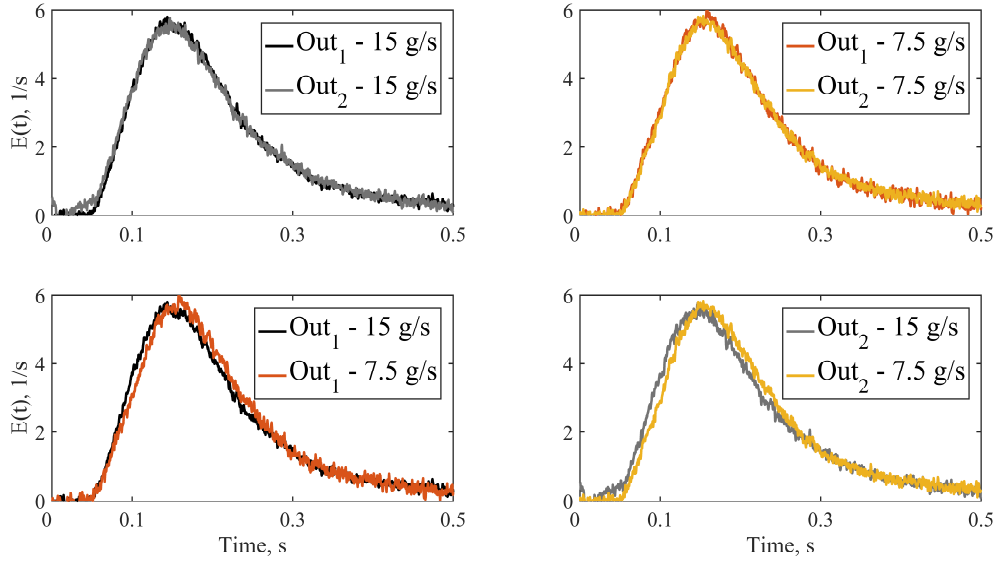


Figure 20: experimental tracer response for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , non-reactive flow.

Figure 20 shows the experimental tracer response collected at the outlet of the SSGT under non-reactive operating conditions. What clearly emerges is that a lower effusion cooling mass flow has a lower impact on the mixing field inside the combustion chamber. For  $m_{cool} = 15 \text{ g/s}$  there is a visible distinction between  $Out_1$  and  $Out_2$ , as the latter shows an earlier rise. Apparently, the presence of an additional flow in the lower part of the combustor might have a “fast bypass” effect, entraining part of the flow and accelerating it towards the exit. This feature is not distinguishable for  $m_{cool} = 7.5 \text{ g/s}$ , where the distributions overlap. The impact of a lower amount of coolant flow for a given measurement position is shown on the lower row of Figure 20. Less cooling air delays the distribution, and this effect is clearer and more pronounced on  $Out_2$ , more sensitive to changes in the lower part of the combustor. These measurements point out the lack of perfect mixing at the exit plane of the combustion chamber, and the relevancy of the two measurement positions in order to assess the influence of cooling air on the mixing behaviour.

Table 3: experimental mean residence time for non-reactive flow

	$m_{cool} = 15 \text{ g/s}$	$m_{cool} = 7.5 \text{ g/s}$
$\tau_1^m$	$0.21 \pm 0.01$	$0.21 \pm 0.01$
$\tau_2^m$	$0.20 \pm 0.02$	$0.21 \pm 0.01$

Table 3 reports the mean residence time (see Equation 21 in section 2.2) calculated for each response shown in Figure 20, together with the uncertainty associated to the experiment. The mean residence time associated with  $Out_2$  is slightly lower than the one calculated for  $Out_1$ , corroborating the statement that

the cooling flow accelerates part of the main flow towards the exit. As already mentioned for Figure 20, this observation does not apply to  $m_{cool} = 7.5 \text{ g/s}$ .

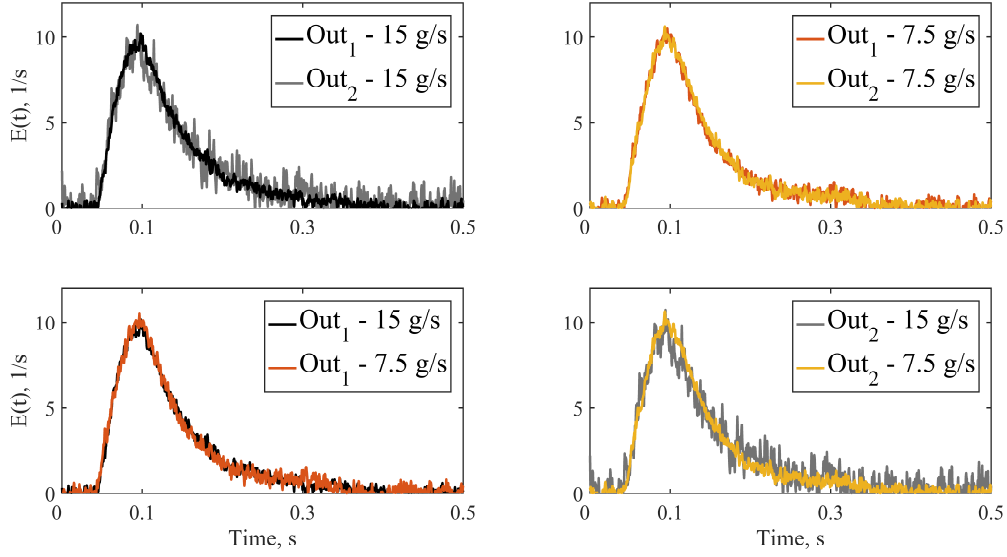


Figure 21: experimental tracer response for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , reactive flow.

Figure 21 shows the comparison among the different tracer responses recorded at the exit of the combustor. The upper row of images shows the two responses for a given mass flow, while the lower row compares the results at the same measurement location for different amounts of effusion air. Figure 21 confirms the effect of a lower quantity of cooling air on the measured responses, though less clear than in the non-reactive case, presumably due to the higher velocities associated to thermal expansion through combustion inside the chamber. A lower amount of effusion air introduced in the system corresponds to tracer responses that almost overlap, whereas there is a clear difference while feeding a higher mass flow of cooling air. This statement is reinforced by the calculated mean residence times reported in Table 4. As for the cold case, reported in Table 3, an appreciable difference is found between  $Out_1$  and  $Out_2$  for  $m_{cool} = 15 \text{ g/s}$ , whereas no difference is calculated for  $m_{cool} = 7.5 \text{ g/s}$ .

Table 4: experimental mean residence time for reactive flow

	$m_{cool} = 15 \text{ g/s}$	$m_{cool} = 7.5 \text{ g/s}$
$\tau_1^m$	$0.13 \pm 0.02$	$0.13 \pm 0.02$
$\tau_2^m$	$0.12 \pm 0.03$	$0.13 \pm 0.01$

These findings are again proposed and amplified in paragraph 3.4, where the CRN model enables a deeper analysis of the data. In this section, the impact of the boundary conditions on the mixing and reactive features of the flow is discussed by comparing the result for each operation point to the reference condition,  $m_{cool} = 15 \text{ g/s}$ .

### 3.3 Chemical Reactor Network

The Chemical Reactor Networks (CRNs) applied to the combustion chamber have been designed exploiting the available experimental data on the test rig ([18], [114]) and testing modelling strategies proposed in the literature, applied in similar situations. At first, a CRN for the cold flow field was designed, based on the mixing characteristics of the different zones identified in the system, as shown in section 3.3.1. A slight modification of the model, motivated and explained in paragraph 3.3.2, was applied to make the CRN suitable to describe both reactive and mixing features of the configuration. In this paragraph, the procedure and the tools exploited to size the CRN model is briefly described. The models are then introduced and explained. The experimental fit is presented for the two benchmark cases introduced before:  $m_{\text{cool}} = 15 \text{ g/s}$  and  $m_{\text{cool}} = 7.5 \text{ g/s}$ .

#### 3.3.1 Cold flow Chemical Reactor Network

The CRN developed to describe the flow features, is shown in Figure 23 (separated parts) and Figure 24 (entire network) for the non-reactive operation. The simple layout is mainly inspired by [67], [68], where a simple network is proposed, that takes the fundamental macro-mixing zones in a model gas turbine combustor into account. Below, Figure 22 depicts the non-reactive flow field of the combustor as a result of PIV measurements from [18]. A high velocity jet-region giving rise to two main recirculation zones (central or Internal Recirculation Zone, IRZ, and a corner or External Recirculation Zone, ERZ) is present, as a typical flow field of a swirling confined configuration, see section 1.2.

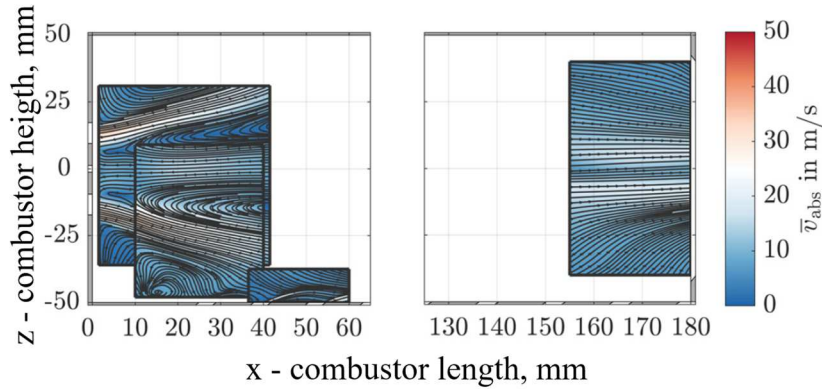


Figure 22: non-reactive flow field of the SSGT, [18].

Taking Figure 22 as a reference of the non-reactive flow field, three main paths form the CRN, see Figure 23. The entire CRN is shown in Figure 24. As shown in Figure 23.a, a PSR is used to represent the IRZ and the ERZ. The jet-like region that occupies the volume between these two recirculation zones is schematized by a series of two PFRs, since a preferential flow direction can be identified. In this region, the recirculated flow merges with the fresh mixture and can either be recirculated or bypass the recirculation zones. Two parallel PFRs are employed to simplify the fluid dynamics of the exit region of the combustion chamber. Here, the flow streamlines mostly follow linear trajectories, which justifies the use of the PFR. The small, upper PFR in the segregated exit region (Figure 23) represents the central part of the mass flowing towards the exit, and the bigger, lower one represents the rest of the volume around it, leaving out just the volume attributed to the lower effusion path. In this way, the designed network is a 2D schematization of the flow in the combustor, with the addition of the effusion cooling path. This path, as illustrated in Figure 23.b, is represented by a series of PFRs, as suggested also in [34], whose volume is estimated from [114]. Three reactors are employed because three zones are identified to exchange flow with the effusion cooling region. This is schematized in Figure 24, where the entire network is shown. As stated earlier, the injection of the seeding to measure the RTD of the system occurs before the combustion chamber. More precisely, the seeding is entrained in the bypass tube, and then mixes with the main air flow rate in the plenum before the swirler.

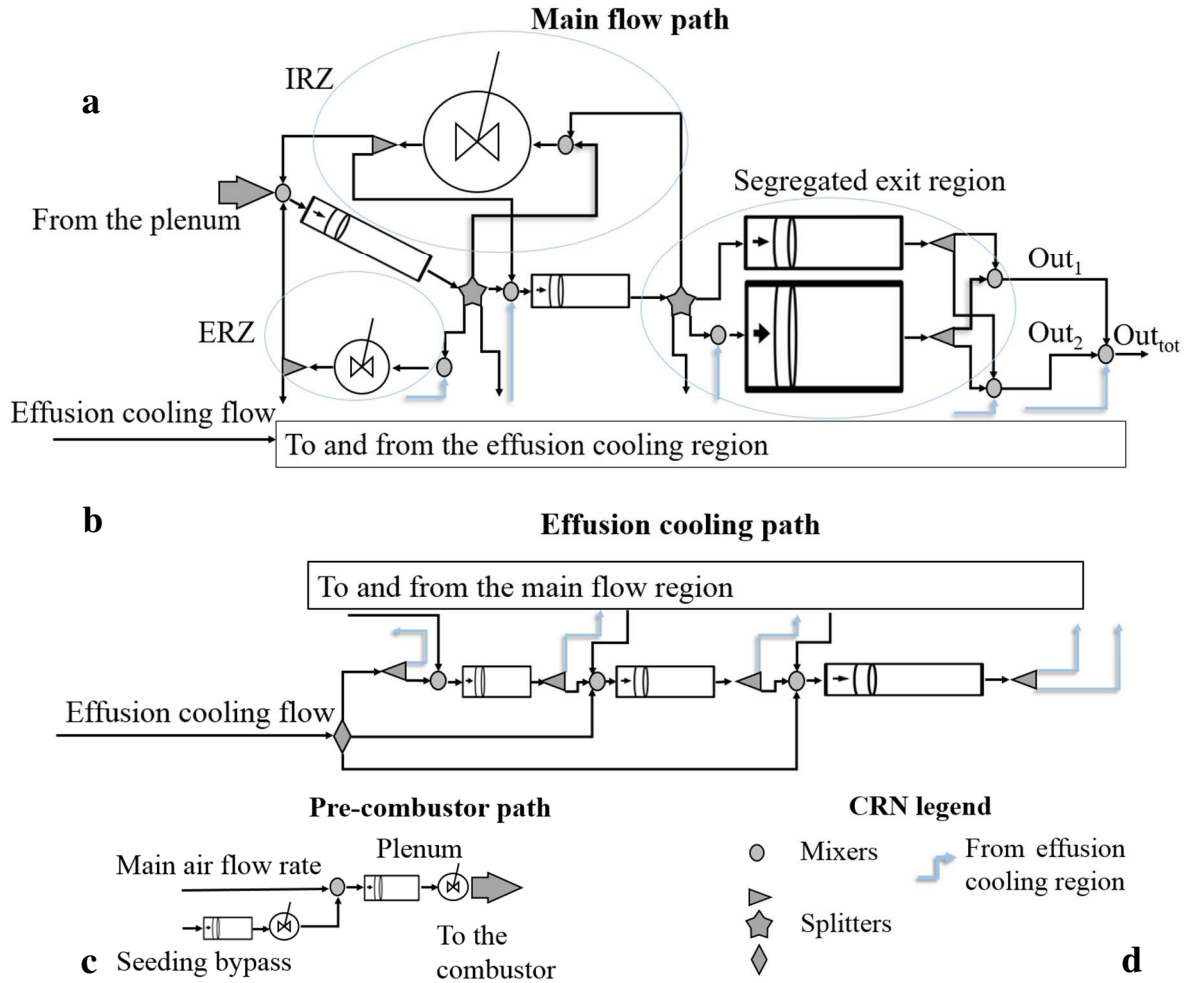


Figure 23: non-reactive flow CRN, represented in terms of main flow paths. **a**, main flow path; **b**, effusion cooling path; **c**, pre-combustor path; **d**, symbols used.

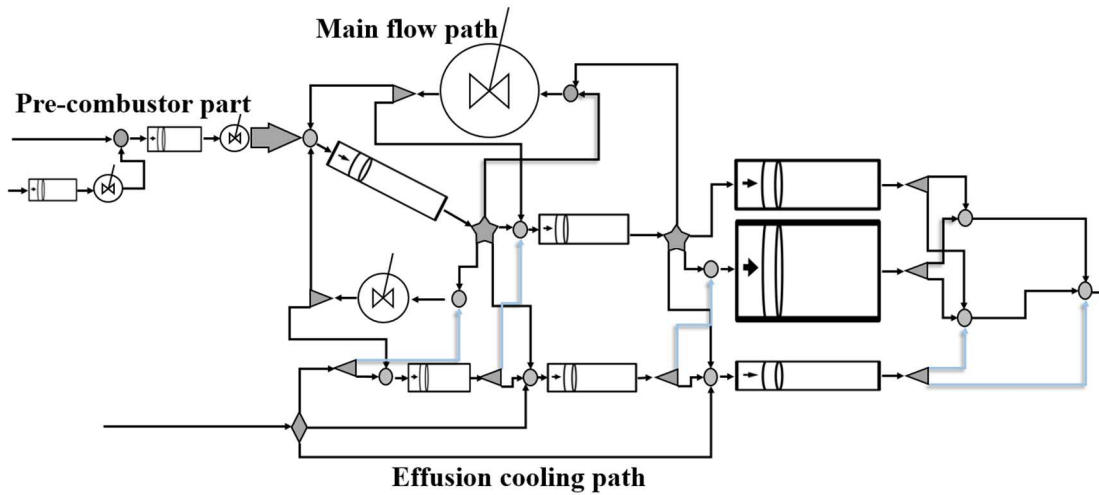


Figure 24: non-reactive flow CRN, entire representation.

This path of the seeding is taken into account in the CRN structure in the following manner: the flow of the fluid in this pre-combustor part translates to a severe broadening of the initial pulse (detailed description in sections 3.3.1.3 and 3.3.2.2), and it is incorrect to still assume a pulse-like input function at the entrance of the combustor. This is indeed clear from the extinction signal collected at the entrance of the combustor (Figure 18 and Figure 19) and makes it necessary to introduce a section of the network

for the pre-combustor path. Therefore, a delay time and an exponential decay time were considered both for the bypass path and for the plenum/swirler part (refer to Figure 11). These characteristic times were part of the optimization procedure for  $m_{cool} = 15$  g/s and  $m_{cool} = 7.5$  g/s, both reactive and non-reactive. They are not part of the optimization procedure for the other investigated cases listed in Table 2: an average value between the optimized ones was used instead, in order to reduce the number of parameters.

The network parameters to be optimized to size the network are the splitting ratios (defined in paragraph 2.2.1) at each illustrated splitter in Figure 23 and Figure 24, obtained by fitting the network response to that of the investigated system. More detailed, the mathematical model of the CRN is implemented in Matlab Simulink® [122] and the dynamic response of the model to the experimental input is fit to the experimental response of the system. An optimization routine from the Matlab Optimization Toolbox is employed. The routine (Figure 9 in paragraph 2.2.1) compares the response of the CRN-system implemented in Simulink®, calculated using the first guess parameters, to the experimental one. The objective function, that must be minimized in order to find the suitable network parameters, is written taking into account the sum of the squared residuals, as in Equation 31:

$$Objective\ function = \sum_{i=1}^n (response_{calculated}(i) - response_{measured}(i))^2 \quad \text{Equation 37}$$

$i$  = sample count. It refers to each time sample that constitutes the experimental curves and the numerical ones.

Both  $Out_1$  and  $Out_2$ , Figure 23, are included in the objective function. Ideally, these two responses combined give the global tracer response of the system, referred in the following as  $Out_{tot}$ .  $Out_{tot}$  is also depicted in Figure 23. It represents the response ideally measured after the exit nozzle of the combustion chamber. This measurement is not available, and this quantity has been obtained as a result of a weighted mean between the distribution  $Out_1$  and  $Out_2$ . The weighting factors have been calculated from the optimization results, as the ratio between the amount of mass flow leaving through a determined outlet with respect to the total mass flow entering the system. Although  $Out_{tot}$  is not involved in the optimization procedure, the agreement of the fit is shown in the following for completeness. Indeed, this distribution is the one employed in the following section 3.4 to comment on the impact of the operating conditions on the mixing behavior of the combustor.

Once the flow rate entering each reactor is known, it is possible to calculate the mean residence time for each component of the network and the gain parameters for each mixer, as described in section 2.2.1. These parameters enable the calculation of the dynamic response of the system.

### 3.3.1.1 Experimental fit

The agreement between the results of the CRN fit and the experimental data for the standard operating point,  $m_{cool} = 15$  g/s, and for the case with lower effusion cooling mass flow,  $m_{cool} = 7.5$  g/s, is presented in Figure 25. Three rows of plots are presented for each situation. The first two rows compare the measured tracer response with the response of the optimized system in Figure 24, for the two sampling outlets  $Out_1$  and  $Out_2$ . The third row in Figure 25 compares the experimental and network-derived  $E(t)$  for  $Out_{tot}$ . As briefly explained in section 3.3.1,  $Out_{tot}$  is the tracer response of the system ideally measured outside its boundaries. This quantity is depicted in the schematic in Figure 23. A measurement of the  $E(t)$  outside the boundaries of the SSGT is not available: the “ $Out_{tot}$  exp.” have been obtained by weighting the experimental data for the two sampling outlets using weighting mass flow coefficients derived from the optimization procedure. The “ $Out_{tot}$  fit” has been calculated in the same way, weighting the fitted curves. In each plot, the tracer response detected shortly after the entrainment of the seeding is also reported, as a visual comparison of the broadening of the signal. This tracer response, also referred to as “Experimental Inlet Pulse”, Exp. Pulse in Figure 25, is normalized in each plot to the maximum of the distribution involved, for graphical reasons. In each graph, the residuum, calculated as the difference between experiments and fit is also reported and denoted wit StD.

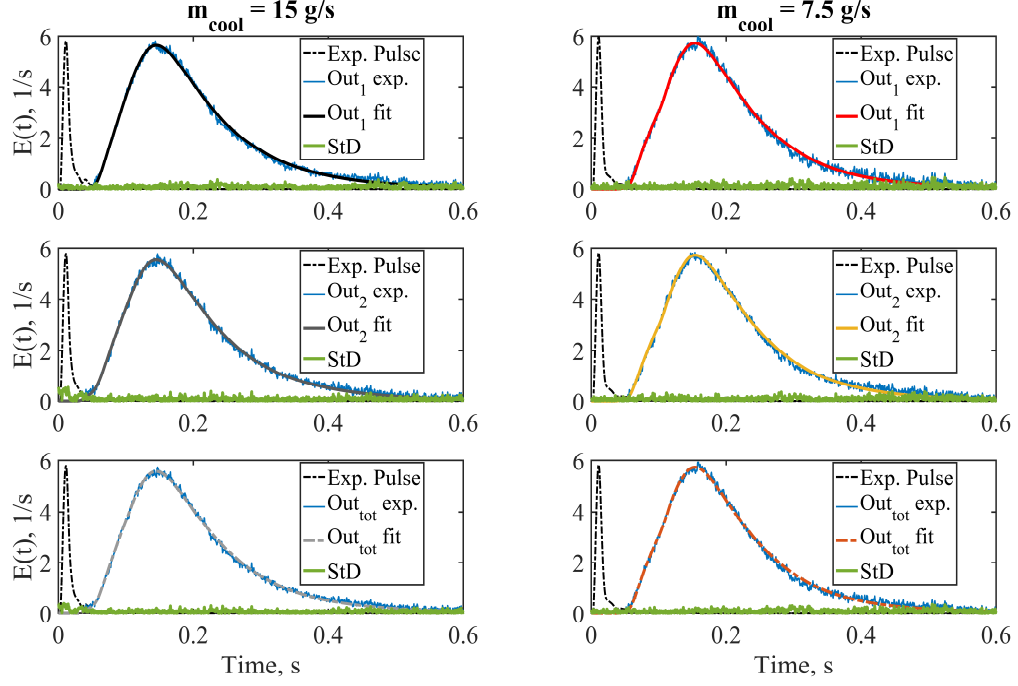


Figure 25: experimental tracer response with superimposed CRN fit, for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , non-reactive operation. The Inlet Pulse is reported for comparison.

To quantify the uncertainty of the network variables and, accordingly, the one of the quantities chosen to describe the differences among the tested cases, the optimization has been carried out for the standard operating point (Table 1) on a single-injection basis. For this task, the single-injection Inlet Pulse was fed to the Simulink<sup>®</sup> program, and the model fitted to the corresponding single-injection  $Out_1$  and  $Out_2$ . The set of optimization values obtained with this procedure have been employed to calculate network-specific parameters (see Table 6) that will be later exploited to describe the effect of the boundary conditions on the RTD. The deviation around the tracer response curves is shown in Figure 26, and the uncertainty on selected parameters is reported in Table 6. The column “Average fit” contains the values extracted from the fit of the average distribution, while “Mean single injection” contains the mean of the values calculated for each injection. The calculated standard deviations will be applied in the following to all the non-reactive CRN fits. Each parameter is explained in Table 5.

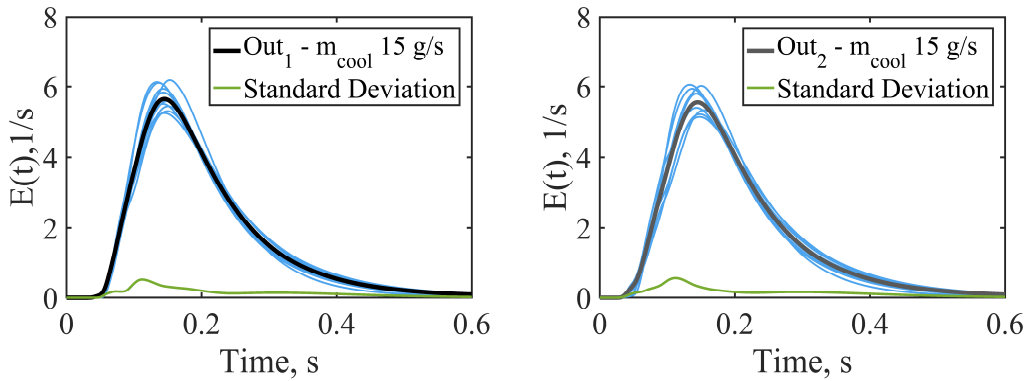


Figure 26: single-injection CRN-fit for non-reactive measurements, in blue, and superimposed average fit. The single-injection optimization is applied on  $m_{cool} = 15 \text{ g/s}$ .

Table 5: model parameters.

$\tau_{i\_response}^m$	Mean residence time calculated according to the tracer response.	$\tau_i^c$	Convective time delay, calculated as the time instant at which the derivative of the distribution becomes higher than a certain threshold.
$\tau_i^m$	Mean residence time calculated according to the extracted RTD (more in 3.3.1.3)	$\tau_i^{0.95}, \tau_i^{0.99}$	Time at which the area below the RTD reaches 95% or 99% of its value. Both characteristic times are reported to comment on the slow characteristic of the distributions.
$\sigma_i^2$	Variance of the distribution, calculated according to the extracted RTD (3.3.1.3)	$\frac{m_{IRZ}}{m_{in\_main}}$	Mass flow recirculated in the IRZ with respect to the mass flow issuing from the inlet nozzle.
$S_i^3$	Skewness of the distribution, calculated according to the extracted RTD (3.3.1.3)	$\frac{m_{ERZ}}{m_{in\_main}}$	Mass flow recirculated in the ERZ with respect to the mass flow issuing from the inlet nozzle.
$\tau_{IRZ}$	Residence time in the IRZ.	$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	Global amount of mass flow mixing into the main flow path from the cooling region.
$\tau_{ERZ}$	Residence time in the ERZ.	$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	Global amount of mass flow mixing into the cooling region from the main flow path.

 Table 6: uncertainties associated with the CRN fit, non-reactive flow,  $m_{cool} = 15$  g/s.

	Average fit	Mean single injection		Average fit	Mean single injection
$\tau_{1\_response}^m$	0.209±0.008	0.208	$\tau_1^c$	0.029±0.002	0.031
$\tau_{2\_response}^m$	0.207±0.009	0.206	$\tau_2^c$	0.011±0.002	0.011
$\tau_{tot\_response}^m$	0.207±0.009	0.197	$\tau_{tot}^c$	0.011±0.002	0.011
$\tau_1^m$	0.081±0.004	0.081	$\tau_1^{0.95}$	0.16±0.02	0.16
$\tau_2^m$	0.079±0.004	0.079	$\tau_2^{0.95}$	0.16±0.03	0.16
			$\tau_{tot}^{0.95}$	±0.02	0.15
$\tau_{tot}^m$	0.072±0.002	0.070	$\tau_1^{0.99}$	0.44±0.02	0.44
			$\tau_2^{0.99}$	0.44±0.02	0.43
$\sigma_1^2$	0.0054±0.0004	0.0052	$\tau_{tot}^{0.99}$	0.43±0.02	0.43
			$\frac{m_{IRZ}}{m_{in\_main}}$	1.3±0.3	1.1
$\sigma_2^2$	0.0055±0.0003	0.0054	$\frac{m_{ERZ}}{m_{in\_main}}$	0.08±0.03	0.07
$\sigma_{tot}^2$	0.0057±0.0003	0.0055	$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	0.30±0.06	0.28
$S_1^3$	5±1	6	$\tau_{IRZ}$	0.011±0.004	0.014
$S_2^3$	5±1	5	$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	0.27±0.05	0.3
$S_{tot}^3$	5±1	5	$\tau_{ERZ}$	0.17±0.09	

### 3.3.1.2 Sensitivity analysis

In addition to the error analysis, a sensitivity analysis is also carried out, to assess the relevancy of selected fit parameters and comment on their effect on the overall fit quality. In the following analysis, some network parameters are selected and arbitrary changed, in order to check their effect on the optimized distributions. The scope of this analysis is to gain confidence in the chosen network by improving the understanding of impact of selected features on the final response. This study is carried out only for the non-reactive flow in order to reduce the complexity of the investigation. The reference operating conditions  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$  are taken into account and the different behaviour is commented based on the specific operating condition.

#### Mixing characteristics of the reactors of the network.

Compartmental Models analysis proved useful in many practical situations, combustion-related and not [47], [52], [68]. Despite its power to simplify complex phenomena, this modelling strategy requires caution: as often pointed out, more than one reactor arrangement might be able to reproduce the response of a given system. A first precaution against this possibility is to measure the RTD between various locations within the investigated reactors [58], in order to be able to match more than one experimental curve. The employment of two outlet measurement locations in this work follows this suggestion. Another strategy, largely employed in combustion studies, makes a joint use of CRN and Zonal Modelling of the flow. In other words, a basic knowledge of the flow features guides the reactors arrangement [47], [56], [63], [67]. In the current work, the response measured at two different locations on the exit plane of the combustion chamber has been used as objective to deduce the CRN parameters. However, the effect of a different choice of the reactor characteristics has then been tested. That is, in one case the optimized model was run on a network comprising just PFR reactors, and in the other case, on a network comprising CSTR reactors only. The results are reported in Figure 27.

Swapping segregated zones for mixed ones has a more severe effect than swapping mixed zones for segregated ones. Precisely, when all the PFRs are replaced with CSTRs, the curve rises earlier (except for  $Out_2, m_{cool} = 15 \text{ g/s}$ ) and is slightly broader, determining a lower distribution. Replacing plug flow zones translates into removing those zones that are responsible for a delay in the response of the system, explaining the earlier onset of the curves. In particular, the replacement of the main flow reactors in the segregated exit region has the main effect on the shape and features of the distributions. This is confirmed by several factors. The first, is the lower impact of the modification of the network on the rising edge of  $Out_2, m_{cool} = 15 \text{ g/s}$ : as discussed in a paragraph 3.4, this distribution is more affected by the mixing of cooling air in the system, determining a “fast-track” path along the combustor due to tracer entrained in the effusion flow. Replacing PFRs with CSTRs does not change the properties of this flow regarding the onset of the curve. This discussion does not apply to  $Out_2, m_{cool} = 7.5 \text{ g/s}$ , because the interaction between the main and effusion cooling flow is not as pronounced as in the previous operating point.

Exchanging mixing zones for segregated ones shows instead a closer resemblance to the optimized one, that confirms the faithfulness to reality of a segregated exit regions and its major impact on a “CSTR” model. Nevertheless, introducing a delay time in regions of the combustor characterized by a distribution of residence times instead translated to a later rise of the response curve and to a higher mean residence time,  $\tau^m$ . The close similarity between the two curves also points out the major impact that the mixing tube has on the broadening of the distribution: the presence of zones that are schematized as perfectly mixed, though correct both from a phenomenological and an optimization point of view, does not significantly contribute to the further broadening of the response curves.



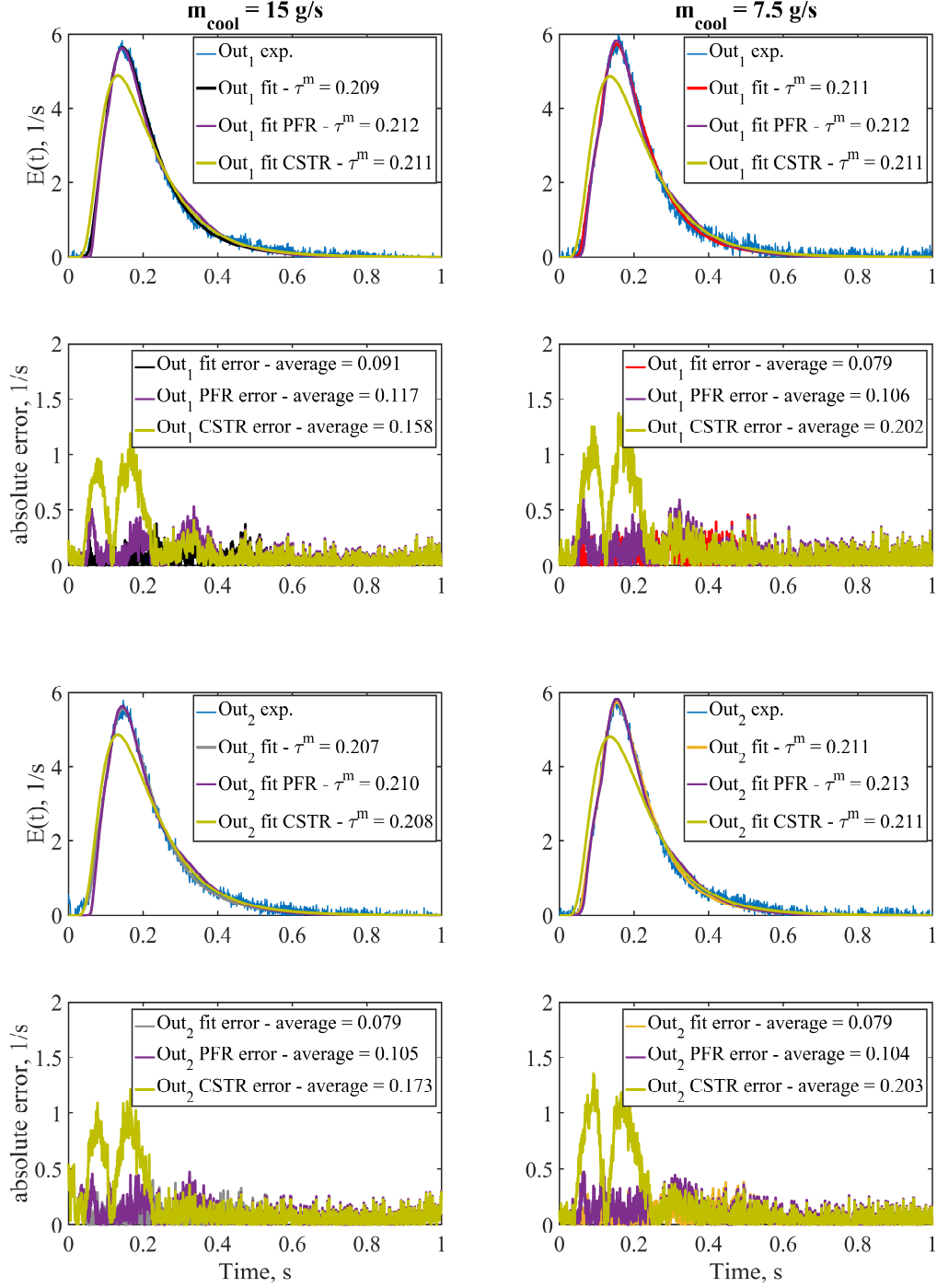


Figure 27: effect of reactors type.

### Effect of the global mass flow from the effusion cooling region to the main flow region.

In the following, the parameters regulating the flow exchange between the effusion cooling region to the main flow region are altered to check their effect on the global response of the system. More precisely, the effect of a reduction of the parameters (minus 25%, 50% and 90%) is investigated. The reason why only a reduction was investigated for these parameters lies in the need to respect the mass balance at each splitter of the network (see section 2.2.1): in this case, an increase in the parameters value was not possible without altering it. From Figure 28, a heavier reduction implies a larger deviation, as clear both from the shape of the distributions (and respective  $\tau^m$ ) and from the deviation between the experimental and calculated response. The overall effect is a progressive delay of the main features like

position of the maximum and falling edge, that in turn stems into higher calculated  $\tau^m$ . This is attributed to the reduced mass exchange from the lower region to the main flow path: in the case of  $m_{cool} = 15 \text{ g/s}$ ,  $m_{cool}$  equals 50% of the main flow, and more than 30% of the global flow. It is therefore not surprising that a lower mass transport in the direction of the main flow (without changing the mass transport from the main flow to the effusion cooling region) results in a slower response. Accordingly, this delaying effect is clearly lower in the other investigated case,  $m_{cool} = 7.5 \text{ g/s}$ . Here, as the amount of cooling air introduced in the system is lower, the effect of a reduced mixing in the cooling path is reduced.

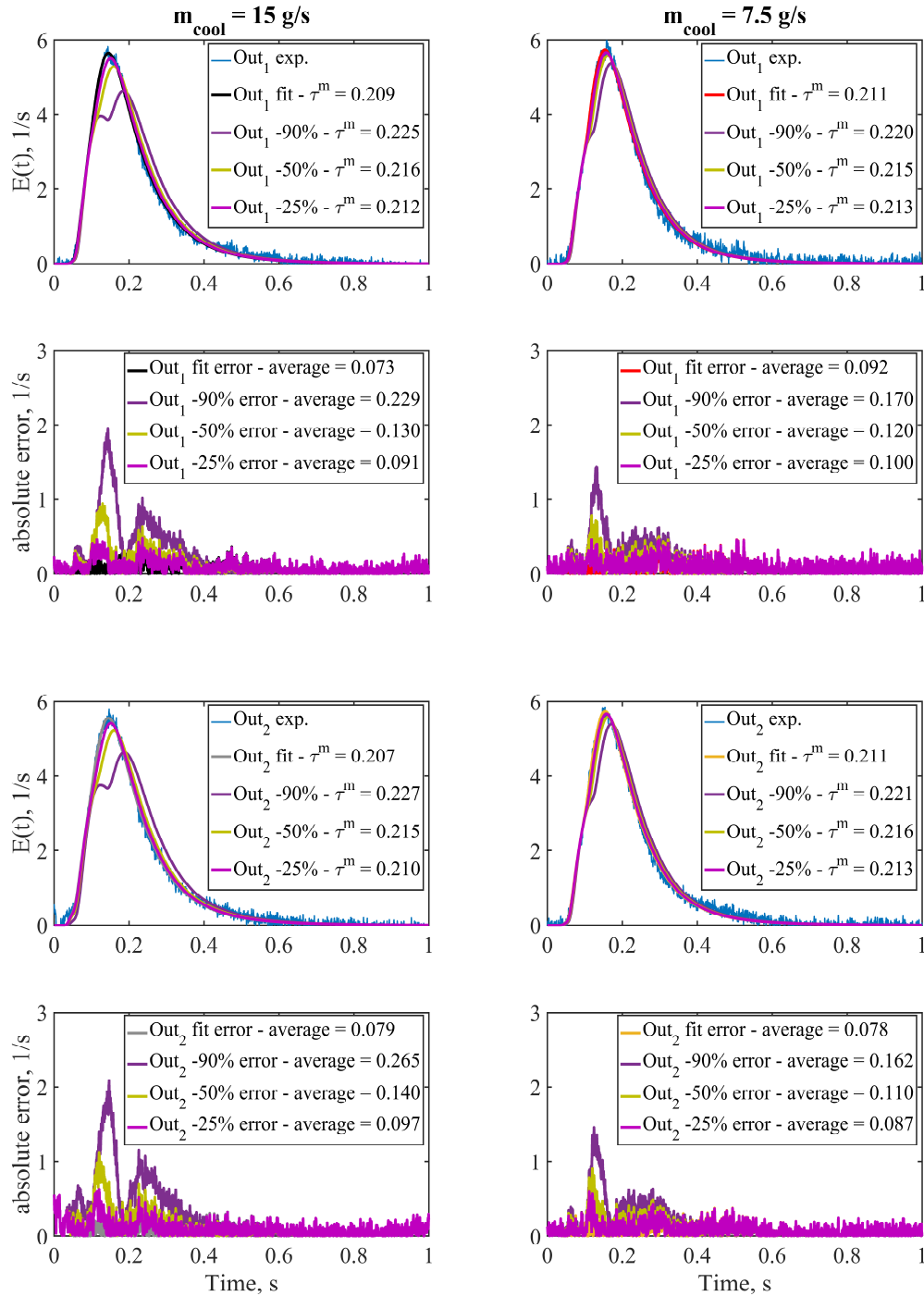


Figure 28: effect of the global mass flow from the effusion cooling region to the main flow region.

Furthermore, a multimodal behaviour with double peaks is encountered, and more pronounced for  $m_{cool} = 15 \text{ g/s}$ . Double subsequent peaks are usually due to parallel phenomena with sufficiently different characteristic times. These peaks show for the case “-90%”, meaning that the exchange of mass flow between the cooling and main path is severely lowered. This lack of mixing and subsequent homogenization of the flow features results in an enhanced segregation of the flow. Hence, it is possible to distinguish the different characteristic times that arise when the flow exits the combustor via the central reactor or the side reactor (see the network schematization, Figure 23 and Figure 24). It is interesting to notice that the rising edge in  $Out_1$  is not significantly altered, as the onset is anyway mainly determined by the main flow. There is instead an effect on the rising edge of  $Out_2$ ,  $m_{cool} = 15 \text{ g/s}$ . As stated earlier, the involvement of the cooling air flow on this curve is the strongest among the four presented curves: it is therefore the case that exhibits the highest sensitivity to a change in the parameters regulating the entrainment of cooling air in the main flow. Indeed, both  $Out_1$  and  $Out_2$ ,  $m_{cool} = 7.5 \text{ g/s}$ , show a weaker responsiveness to this factor, clear from the calculated  $\tau^m$  and deviation.

#### **Effect of the global mass flow from the main flow region to the effusion cooling region.**

The sensitivity analysis carried out now shows the effect of a reduction of the parameters involved in the entrainment of the flow from the main path to the effusion cooling on the calculated tracer response. The results are shown in Figure 29. The consequence is a faster distribution, in that a higher flow rate yields a lower  $\tau^m$ .

#### **Effect of the mass flow recirculated in the ERZ.**

The results of this analysis are shown in Figure 30. The network parameter responsible for the flow entrained in the ERZ was increased by 10% and decreased by 50% and 90%. The 10% increase has no appreciable effect on the shape of the distribution, or on the parameters chosen to carry out the comparison ( $\tau^m$  and the deviation between the experimental and the calculated curves). A decrease in the recirculated mass flow leads to faster distributions because more flow is heading towards the exit of the combustor, reducing the passing time along its length.

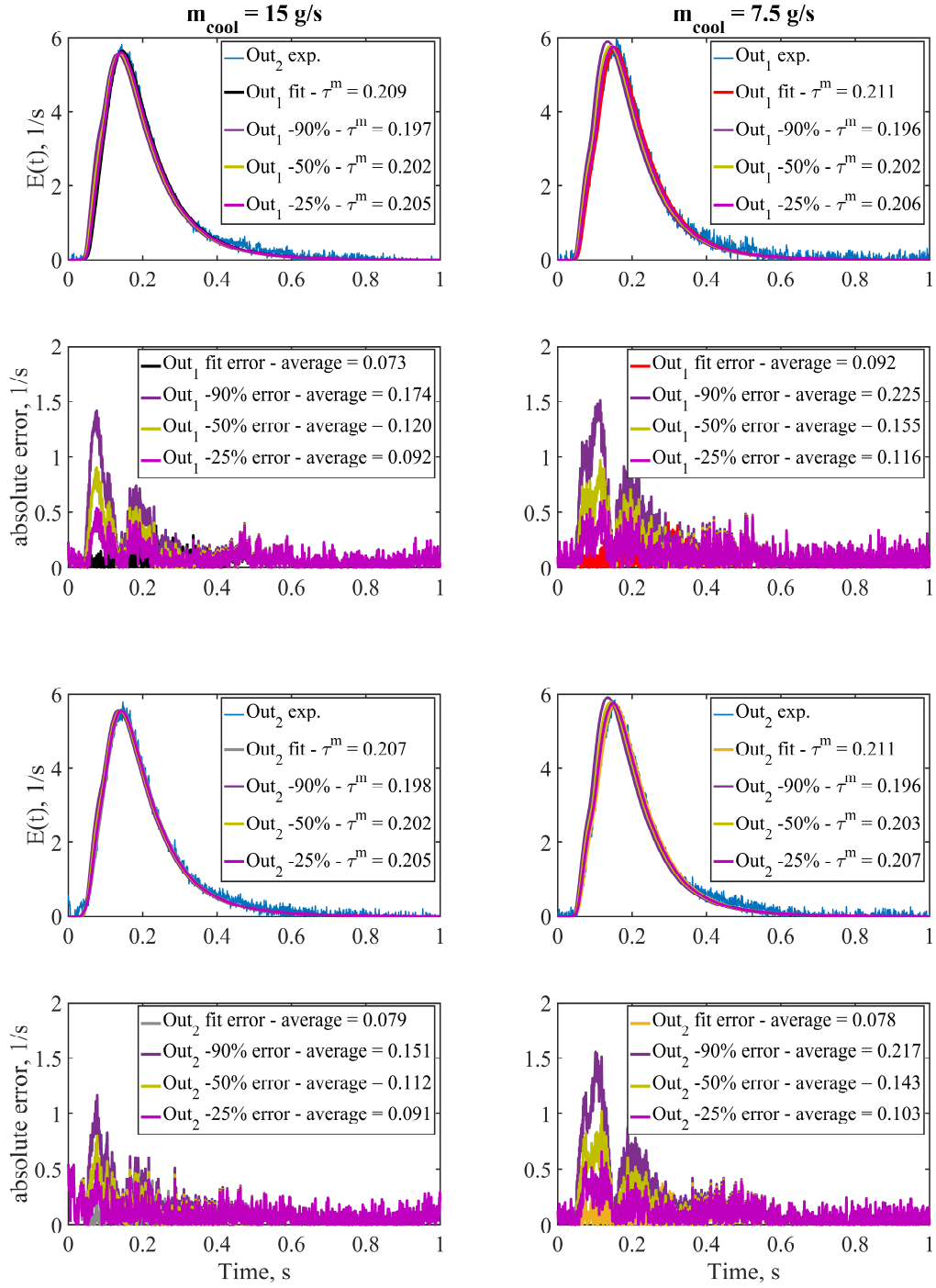


Figure 29: effect of the global mass flow from the main flow region to the effusion cooling region.

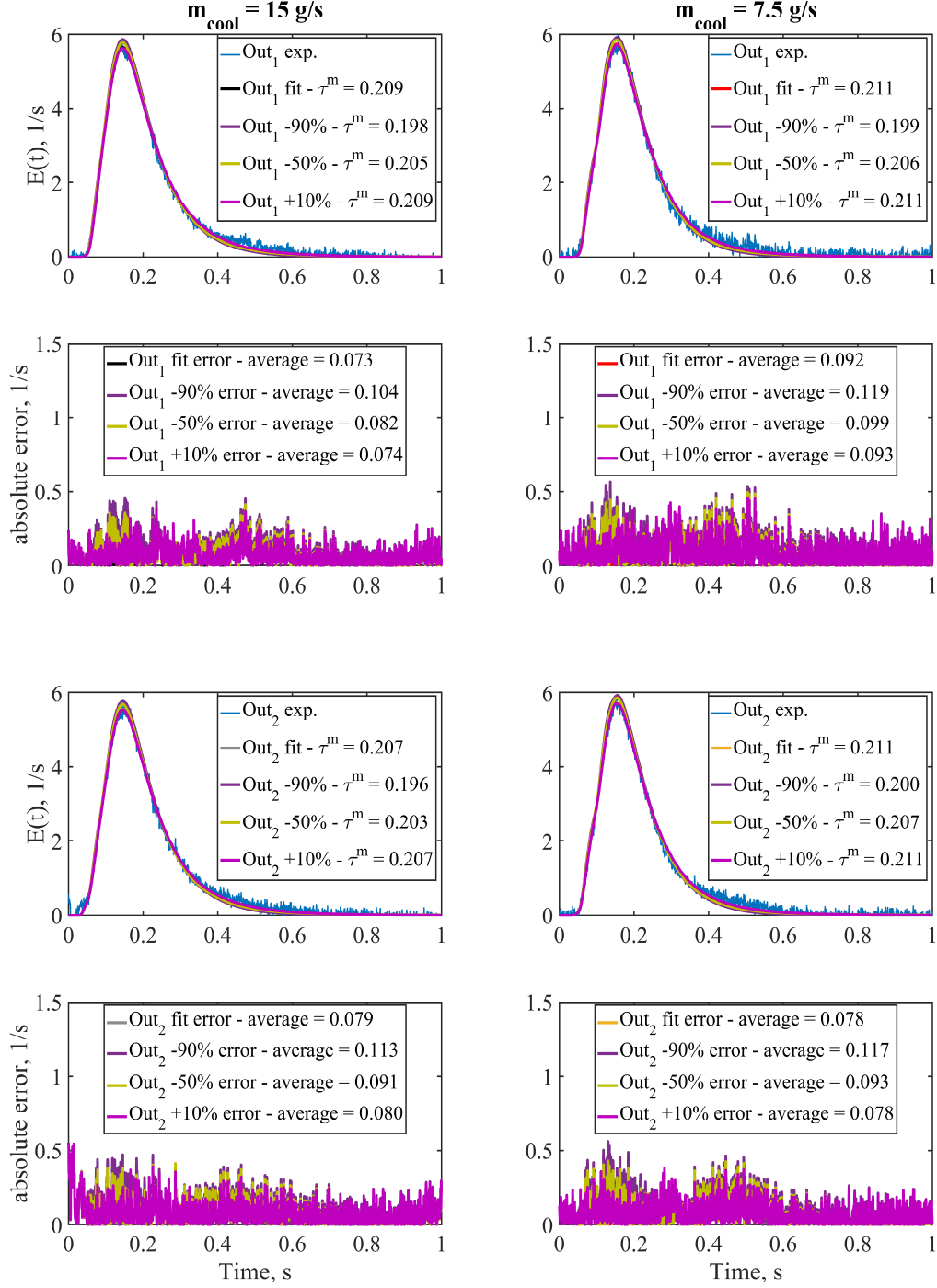


Figure 30: effect of the global mass flow recirculated in the ERZ.

### Effect of the global mass flow recirculated in the IRZ.

To carry out this last comparison, the network parameters regulating the flow entrained in the IRZ were increased by 10% and decreased by 50% and 90%. The results of this analysis are shown in Figure 31. The 10% increase has a minor effect on the shape of the distribution and on the  $\tau^m$ , though clear from the higher deviation between experiments and calculations. A decrease in the recirculated mass flow leads to faster distributions because more flow is heading towards the exit of the combustor, reducing the passing time along its length. There is no appreciable difference between the two operation points

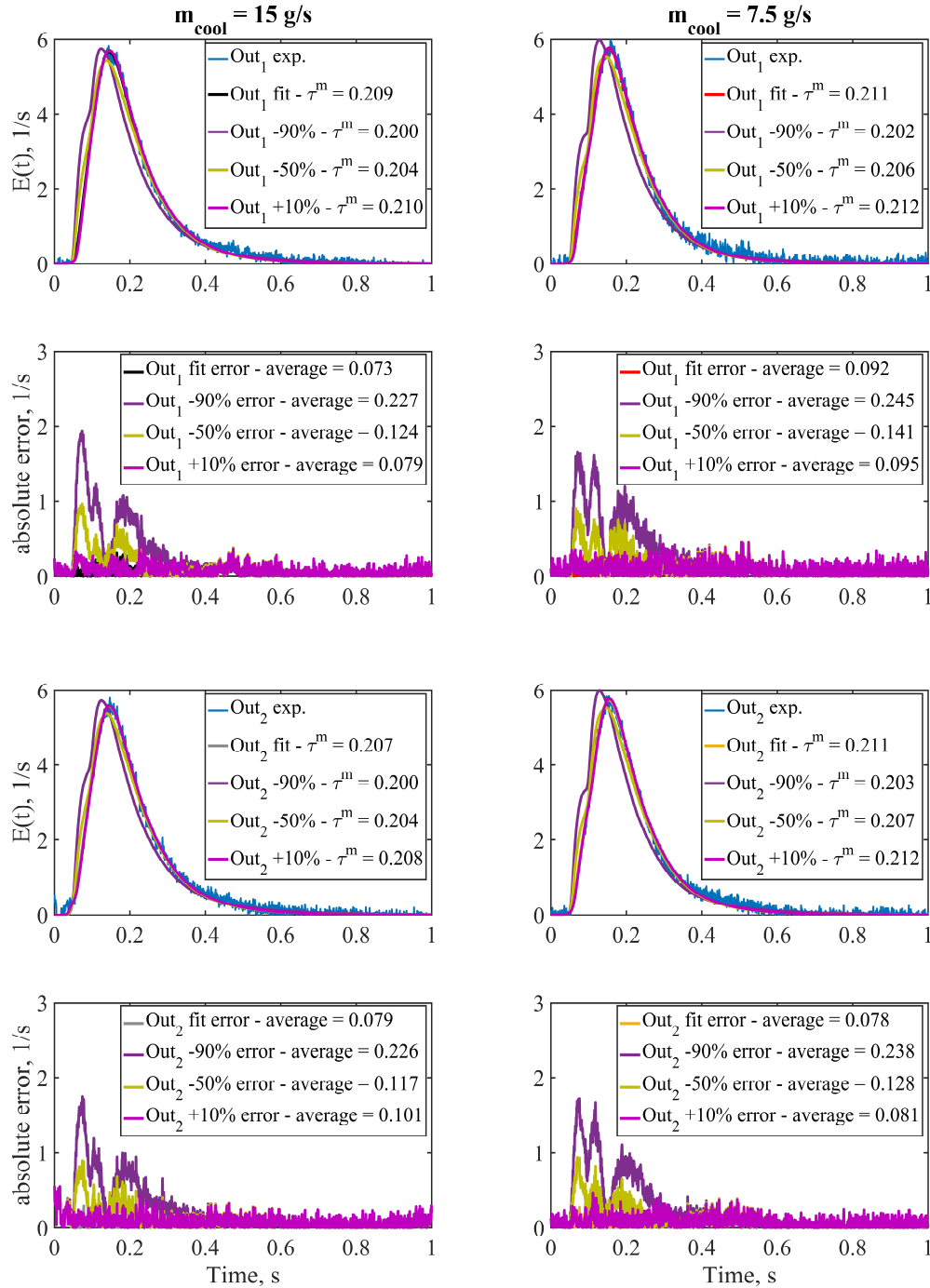


Figure 31: effect of the global mass flow recirculated in the IRZ.

examined, or between the two measurement locations for a given point of operation. The clearer consequence for a reduction of the IRZ flow compared to a reduction of the ERZ flow is attributed to the different value of the characteristic times in these two areas. Characteristic residence times in ERZs are usually larger than residence times in IRZs (shown also in [68]). A higher mixing residence time implies a lower peak concentration and an RTD distributed over longer periods, making it less straightforward to appreciate the differences. For the same reason, the situation is clearer if the  $\tau$  calculated for a certain reactor has a lower value. Furthermore, a change in the ERZ flow directly alters the dynamic of the system only in the first part of the combustor. On the other side, increasing or lowering the mass flow recirculated in the IRZ flow directly affects both initial part and exit zone of the combustion chamber. This is an additional explanation for the stronger impact that the IRZ flow has on the overall flow behaviour.

### 3.3.1.3 RTD extraction from tracer responses

According to RTD theory [36], [40], [48], only the response to a pulse input function can, strictly, be called RTD or  $E(t)$ . In the hypothesis that the experimental pulse fed to the system during the experiments (in Figure 18 and Figure 19) is a close-to-ideal input function, it still yields the RTD of a system that comprises both the combustion chamber and the pre-combustor path. As already pointed out, this path plays a major role on the broadening of the pulse input, making it unfeasible to invoke the closed-vessel-boundary condition that would make it possible to claim that the tracer response is indeed the  $E(t)$  of the system [36].

Therefore, in the following, the actual RTD, of the system is deduced. This strategy considers the CRN model after optimization of the network values. In order to consider only the response of the combustion chamber, the model is deprived of the pre-combustor path and initialized with a numerically generated pulse input instead of the experimental curve. The obtained response, i.e. the response to an ideal pulse of a system comprising the combustor alone, is, strictly, the RTD or  $E(t)$  of the combustion chamber under investigation.

A comparison between the tracer responses and the RTDs is reported in Figure 32. In the figure, both the simulated pulse input (dark blue) and the resulting RTD (in dark green) are shifted in a way that the simulated pulse input and the tracer response after the pre-combustor path (called “Mixing tube” in Figure 32 and corresponding to “Combustor Inlet” in Figure 18 and Figure 19) start at the same time. These two signals are both representative of the state at the entrance of the combustion chamber, and the difference between a response that has already experienced mixing and a pulse input is better visualised in the hypothesis that they start at the same time. The experimental, as well as the numerical pulse are normalized to the maximum of the mixing tube signal, whereas the RTD is normalized on the maximum of the corresponding  $Out_i$  fit. This is necessary for representation purpose: each calculated  $RTD_i$  in Figure 32 is significantly shorter than the respective tracer evolution, stemming from a sharp input function without previous broadening. This feature results in higher  $E(t)$  values due to the area normalization of the distribution, preventing a qualitative comparison, as the one shown in Figure 32. From the figure, the pre-combustor path has clearly a strong impact on the dynamics of the system. The non-ideal entrainment of the seeding in the bypass tube (long tail of the experimental pulse) and the mixing in the plenum before the burner outlet make it possible for a broader signal to enter the combustor, severely stretching the exit distributions and the characteristic times.

Owing to the significant difference between the tracer response and the  $E(t)$  calculated from a numerical pulse, the effect of the operating condition on the RTD of the combustor presented in the next chapters (see next 3.4.1) are addressed referring to the calculated closed-vessel RTD  $_{tot}$  as shown in Figure 32.

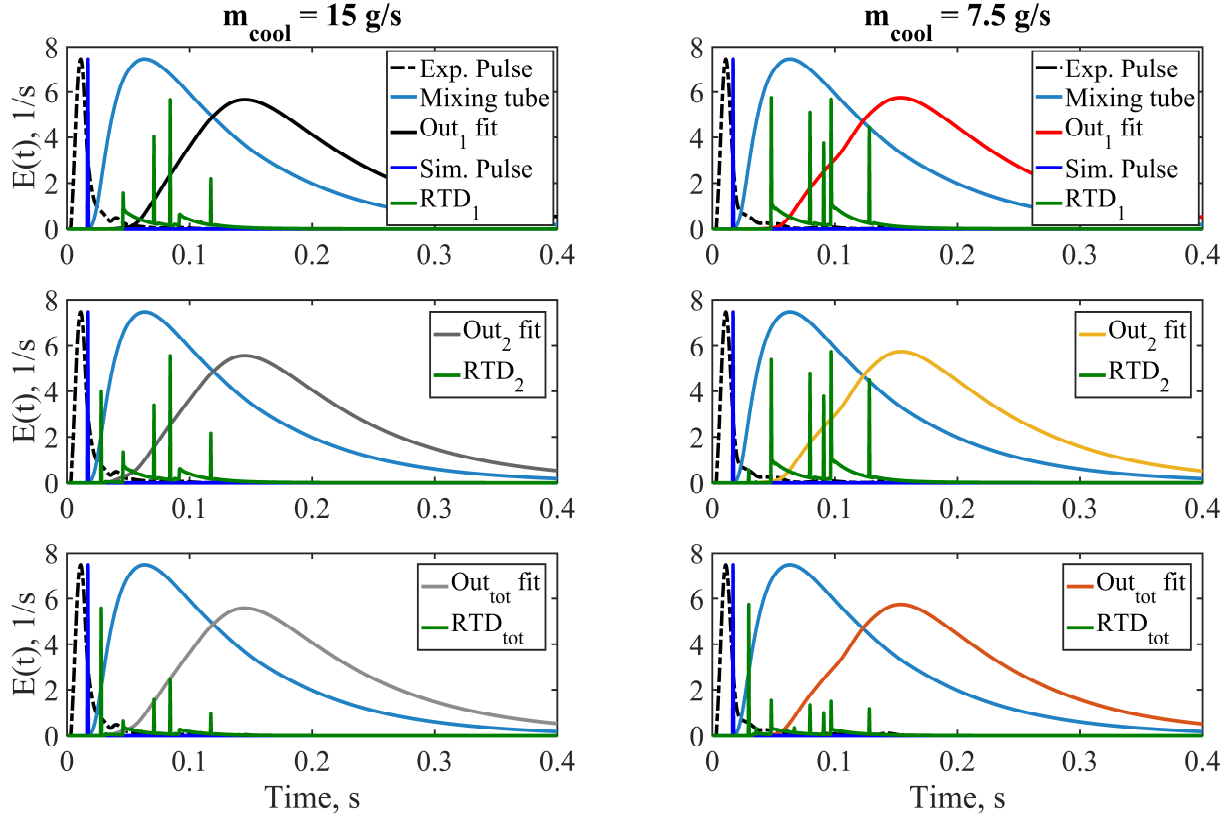


Figure 32: comparison between tracer response and RTD.

### 3.3.2 Reactive flow Chemical Reactor Network

The model applied to the fluid dynamic and kinetic modelling of the gas turbine combustor is shown in Figure 33 and Figure 34. Figure 33 shows the different sections of the CRN, while Figure 34 shows the global model. The non-reactive network model has been slightly modified to capture the impact of combustion on the overall flow field, i.e. on the macro mixing zones inside the system. This modification considers zones with a similar mixing behaviour triggered by the presence of a reaction zone. As for the cold flow, three main paths, illustrated in Figure 33, form the CRN, entirely shown Figure 34.



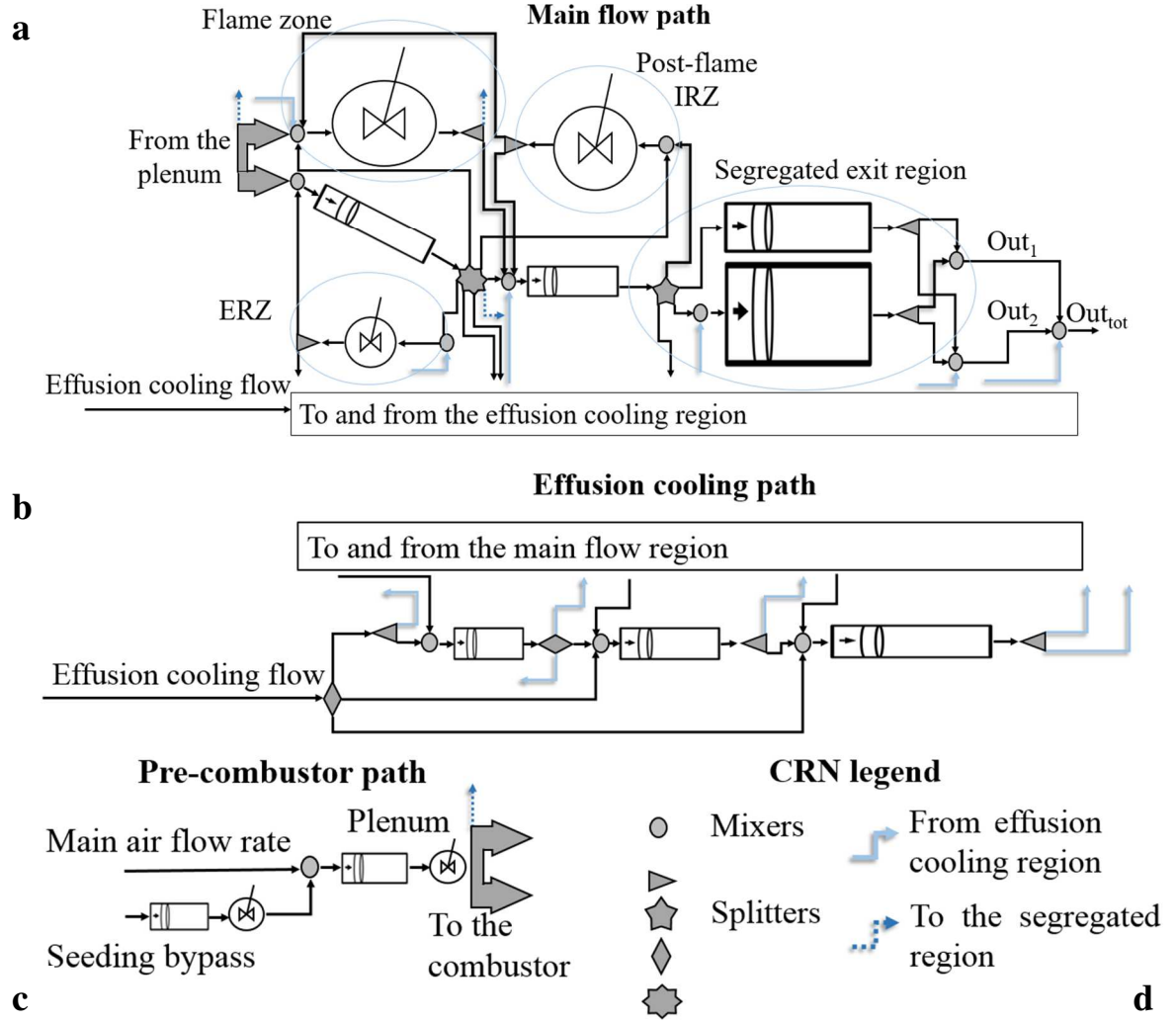


Figure 33: sketch of the CRN employed to fit the reactive flow measurements. **a**, main path; **b**, effusion cooling path; **c**, pre-combustor path; **d**, explanation of the symbols used.

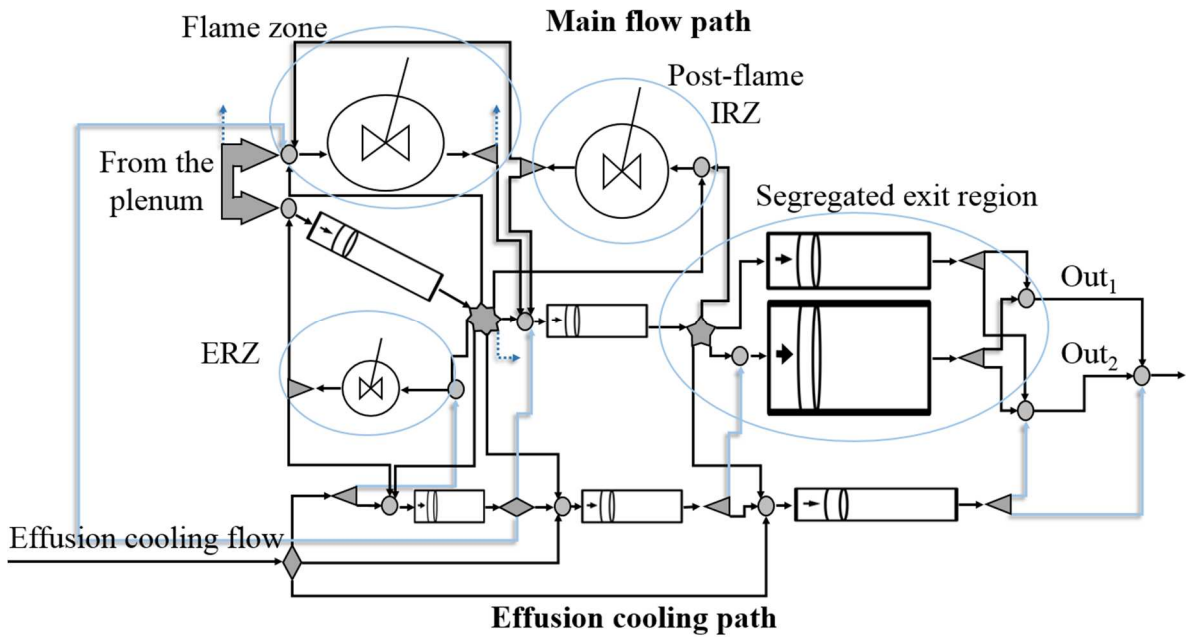


Figure 34: complete sketch of the CRN employed to fit the reactive flow measurements.

Guided by experimental data [18], [114], displayed in Figure 35 and Figure 36, the flame zone was taken as the zone indicated in Figure 36. Therefore, one single zone describes both the flame that stabilizes in the shear layer between the recirculation zones and a portion of the inner recirculation zone. This schematization is encouraged by several works: in [57], [59], [85], [123], the first part of a swirling-flow combustor is simplified by using one single stirred reactor to represent it, due to the high turbulence intensity and strong mixing. After the flame, another CSTR represents the remaining portion of the combustor that can be considered as a stirred region. This stirred region identified after the flame is referred to as post-flame IRZ. A corner recirculation zone develops in the first part of the combustor called ERZ and is as well schematized by a CSTR.

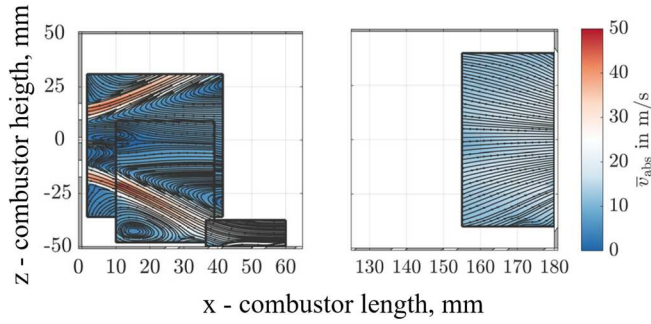


Figure 35: Velocity magnitude and streamlines at partially premixed operation. Reacting flow field [18].

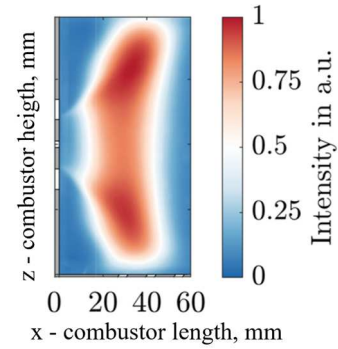


Figure 36: Time averaged chemiluminescence of the fully-premixed flame [18].

A jet-like region, schematized by a series of two PFRs, occupies the volume between these two recirculation zones. In this jet region, the recirculated flow merges with the fresh mixture and can either be recirculated or bypass the recirculation zones. Two parallel PFRs are employed to simplify the fluid dynamics of the exit region of the combustion chamber. Here, the flow streamlines mostly follow linear trajectories [18] which justifies the use of the PFR. The effusion cooling path, which is shown in Figure 33.b, is represented by a series of PFRs, as suggested also in [34]. As for the cold flow CRN, the pre-combustor path is also accounted for.

### 3.3.2.1 Experimental fit – Residence Time Distribution

The agreement between the fit and the experimental data is shown in Figure 37, while Table 7 quantifies the uncertainty of the network variables and the quantities chosen to describe the differences among the tested cases, accordingly.

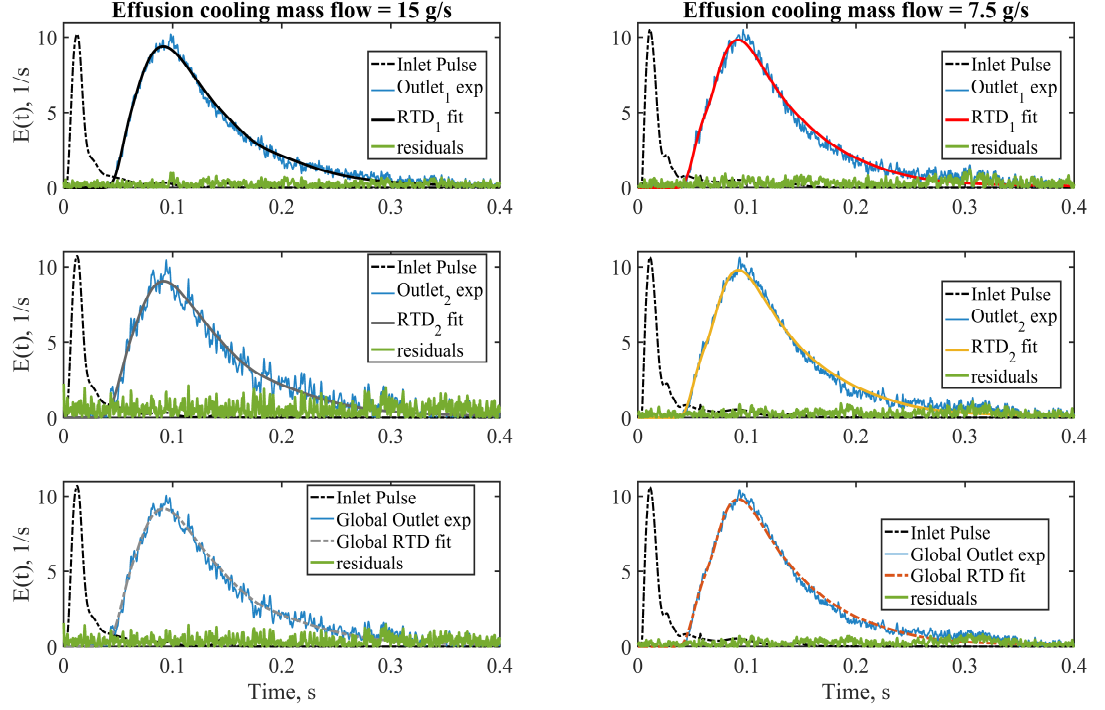


Figure 37: experimental tracer response with superimposed CRN fit, for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , reactive flow. The Inlet Pulse is reported for comparison.

As explained in 3.3.1.1, the uncertainty was calculated using as model input the single-injection Inlet Pulse. The response of the system to each single-injection Inlet Pulse was evaluated and fitted to the corresponding single-injection experiments,  $Out_1$  and  $Out_2$ , by the Simulink® program. The parameters considered for the uncertainty evaluation in Table 7 are explained in Table 5.

Table 7: uncertainties associated with the CRN fit, reactive flow,  $m_{cool} = 15 \text{ g/s}$ .

	Average fit	Mean single injection		Average fit	Mean single injection
$\tau_{1\_response}^m$	$0.13 \pm 0.05$	0.11	$\tau_1^c$	$0.010 \pm 0.002$	0.012
$\tau_{2\_response}^m$	$0.14 \pm 0.05$	0.12	$\tau_2^c$	$0.001 \pm 0.002$	0.003
$\tau_{tot\_response}^m$	$0.13 \pm 0.05$	0.10	$\tau_2^c$	$0.001 \pm 0.002$	0.003
$\tau_1^m$	$0.0260 \pm 0.006$	0.026	$\tau_1^{0.95}$	$0.05 \pm 0.03$	0.06
$\tau_2^m$	$0.026 \pm 0.005$	0.027	$\tau_2^{0.95}$	$0.05 \pm 0.03$	0.07
$\tau_{tot}^m$	$0.018 \pm 0.003$	0.017	$\tau_{tot}^{0.95}$	$0.041 \pm 0.005$	0.043
$\sigma_1^2$	$0.0013 \pm 8 \times 10^{-4}$	0.0011	$\tau_1^{0.99}$	$0.20 \pm 0.09$	0.16
$\sigma_2^2$	$0.0016 \pm 9 \times 10^{-4}$	0.0017	$\tau_2^{0.99}$	$0.22 \pm 0.08$	0.20
$\sigma_{tot}^2$	$0.0010 \pm 1 \times 10^{-4}$	$8 \times 10^{-4}$	$\tau_{tot}^{0.99}$	$0.13 \pm 0.03$	0.12
$S_1^3$	$8 \pm 4$	10	$m_{IRZ}$	$6.5 \pm 0.7$	7
$S_2^3$	$8 \pm 3$	8	$m_{in\_main}$		
$S_{tot}^3$	$10 \pm 2$	10	$m_{ERZ}$	$0.15 \pm 0.05$	0.15
$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	$0.43 \pm 0.05$	0.47	$m_{in\_main}$		
$\tau_{ERZ}$	$0.03 \pm 0.01$	0.03	$m_{flame}$	$0.97 \pm 0.03$	0.98
			$m_{in\_main}$		
			$m_{cooling \rightarrow ma}$	$0.18 \pm 0.03$	0.2
			$m_{total\_feed}$		
			$\tau_{IRZ}$	$5.8 \times 10^{-4} \pm 7 \times 10^{-5}$	$5.5 \times 10^{-4}$
			$\tau_{flame}$	$0.0031 \pm 1 \times 10^{-4}$	0.0031

The single-injection variation of the fits is shown in Figure 38. There is an evident double-peak behaviour observed in one single-injection only. According to the overall behaviour of the set of single-injections, this phenomenon is attributed to a random uneven distribution of the tracer, and it is not believed to represent a relevant macromixing feature of the system under investigation.

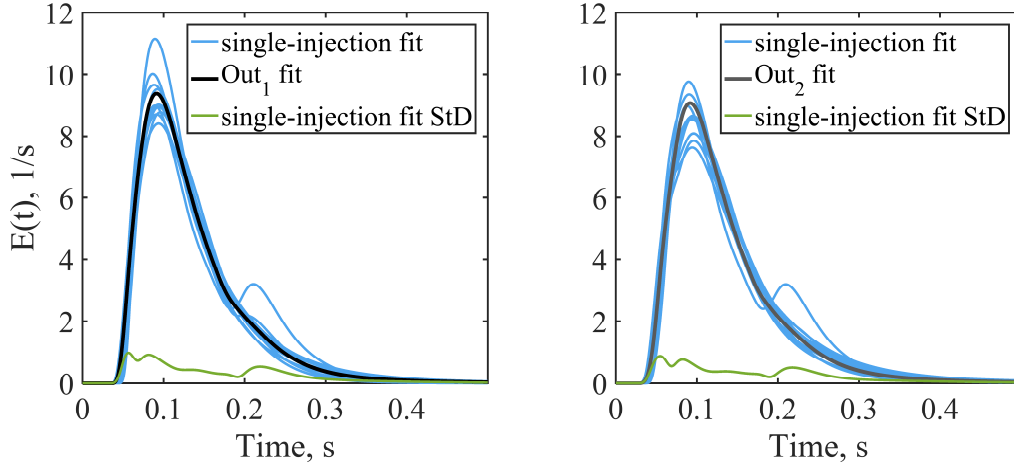


Figure 38: single-injection CRN-fit for reactive measurements, in blue, and superimposed average fit. The single-injection optimization is applied on  $m_{cool} = 15 \text{ g/s}$ .

### 3.3.2.2 RTD extraction from tracer responses

The RTD, or  $E(t)$ , during reactive operation is deduced as already done in the previous paragraph 3.3.1.3. In order to consider only the response of the combustion chamber, the model is deprived of the pre-combustor path and initialized with a numerically generated pulse input instead of the experimental curve. The outcome of this procedure is, strictly, the RTD of the combustor [36]. A comparison between the tracer responses and the RTDs is reported in Figure 39.

In the figure, both the simulated pulse input (dark blue) and the resulting RTD (in dark green) are shifted in a way that the simulated pulse input and the tracer response after the pre-combustor path (called “Mixing tube” in Figure 39 and corresponding to “Combustor Inlet” in Figure 18 and Figure 19) start at the same time. These two signals are both representative of the state at the entrance of the combustion chamber, and the difference between a response that has already experienced mixing and a pulse input is better visualised in the hypothesis that they start at the same time. The experimental, as well as the numerical pulse are normalized to the maximum of the mixing tube signal, whereas the RTD is normalized on the maximum of the corresponding  $Out_i$  fit. As explained in section 3.3.1.3, this is necessary for representation purposes. The strong impact of the pre-combustor path on the dynamics of the system is once again confirmed.

As established for the analysis of the cold flow results, the calculated RTDs (green curves in Figure 39) will be employed in the following to comment on the impact of the operative conditions on the mixing characteristics of the system. Except for the two reference cases,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ , only the global RTD is considered for comparison.

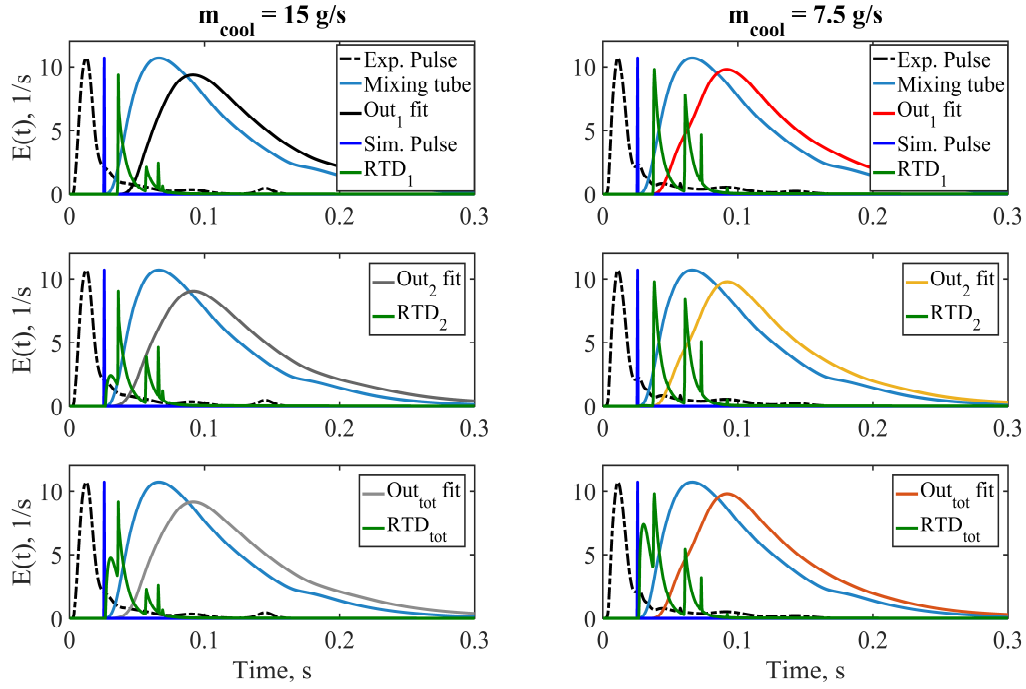


Figure 39: comparison between calculated RTDs and tracer responses for the reactive flow with varying effusion cooling massflow.

### 3.3.2.3 Experimental fit – carbon monoxide prediction

The following figures, Figure 41 and Figure 42, illustrate the comparison between the kinetic results of the CRN in terms of CO concentration and experimental measurements [121]. Here, measured and calculated profiles inside the combustor are compared, whose radial and axial locations are better highlighted in Figure 40. Before continuing with the comparison, a clarification to aid the understanding of the reported species predictions: zones represented by CSTRs give as result a single value of species concentration, by virtue of the basic hypothesis behind this reactor explained in section 2.1.1; whereas a PFR returns an evolution along its reaction coordinate, that can be regarded as a spatial coordinate and as an evolution over time, illustrated in paragraph 2.1.2.

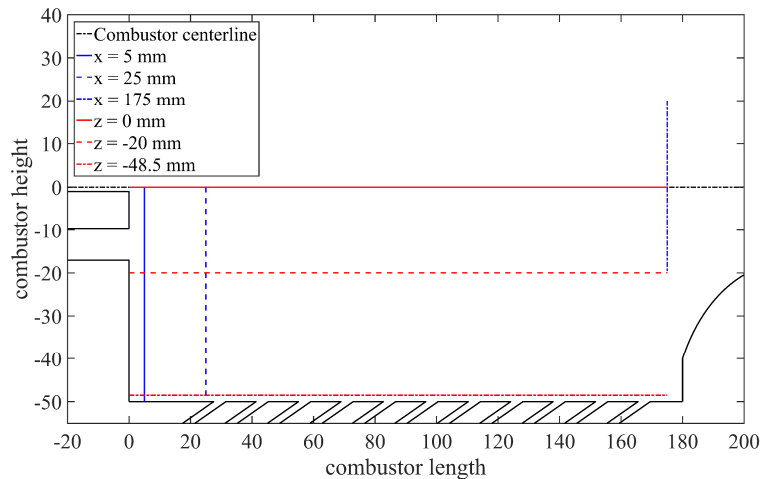


Figure 40: sketch of the lower half of the flame tube. Radial (blue) and axial (red) location used for the following comparison are highlighted.

The overall agreement is good for both investigated operating conditions, see Figure 41 and Figure 42. Several kinetic mechanisms are tested: the two-step combustion mechanism from Ansys Fluent® [124], the GRI 3.0 [125], the C1 – C4 kinetic mechanism with NO<sub>x</sub> formation [126]–[129] and the Aramco mechanism [130]. Except for the two-step mechanism, which fails to correctly reproduce the trends, the

other mechanisms do not show severe discrepancies among each other. The following discussion about the comparison with experimental data refers to the results obtained with the  $C1 - C4$  mechanism. This kinetic scheme is the selected one to carry out the kinetic calculations for every operating condition investigated in section 3.4.2. The choice is based on its overall better agreement to the experimental data with respect to the *GRI 3.0* and its ability to complete the kinetic calculation for each CRN approximately 5 times faster with respect to the Aramco mechanism. Nonetheless, in some cases the *RNA* software, introduced in section 2.2.2, failed to reach convergence in a reasonable time employing the  $C1 - C4$  mechanism. The *GRI 3.0* was therefore preferred to cover those cases, by virtue of the similar prediction between the two mechanisms.

For the following discussion on the comparison between experiments and kinetic calculations, Figure 33 - Figure 36 are taken as reference for the zonal modelling. The profiles are illustrated in Figure 40, Figure 41 and Figure 42. Figure 41 depicts the axial profiles, starting from  $z = 0 \text{ mm}$ , whereas Figure 42 shows the radial profiles, starting from  $x = 5 \text{ mm}$ .

In Figure 41, starting from the left side for  $z = 0 \text{ mm}$ , and proceeding along the combustor length the CO amount produced in the zone that accounts for the flame and the first part of the IRZ is plotted. The calculated mole fraction value appears higher in the flame zone with respect to experiments. This slight discrepancy stems from the employment of a single macro-zone to outline this region, where formation from the flame stabilizing in the shear layer between the recirculation zones, recirculation and further reaction of the combustion intermediates take place. Because of the intense mixing characteristics and the coupled reactive evolution, several researchers recognize this zone to be representable by one sole CSTR [57], [59], [86], [123]. This possibility also supports the need to employ, if possible, macro-mixing zones, when approaching the problem using RTD-driven compartmental models. Macro zones chosen for their fluid dynamic characteristic reduce the number of parameters necessary for the optimization, making it more reliable and able to mirror the underlying phenomena inside the system under investigation. These two reasons are behind the choice of a unique reactor for the flame and the first part of the IRZ. Nonetheless, this choice translates in a value of CO mole fraction that is average between those that characterize this region (0.004 in the flame region and 0.001 in the early IRZ, for  $m_{\text{cool}} = 15 \text{ g/s}$ ). To support what just stated, the profile  $z = -20 \text{ mm}$  shows a better agreement between experiments and modelling than  $z = 0 \text{ mm}$  and  $x = 5 \text{ mm}$  (where the first zone extends until  $-10 \text{ mm}$ ). Going back to the centreline plot at  $z = 0 \text{ mm}$ , after the flame length (approximately  $50 \text{ mm}$  [18]) there is the post-flame IRZ, where the additional time available for reaction and the intense mixing lower the CO concentration. Its value increases again reaching the segregated exit region of the combustor: here flow bypasses from the burner, flame and jet region deliver unreacted CO and  $\text{CH}_4$  that react further. The profiles  $x = 5 \text{ mm}$  and  $x = 25 \text{ mm}$  further clarify the CO formation in the jet region and in the ERZ. Until  $x = 25 \text{ mm}$  the jet region exhibits an increasing CO amount forming along its length due to the proceeding reaction: this region is represented by the interval  $-20 < z < -10$  in  $x = 5 \text{ mm}$ , and  $-32.5 < z < -25$  in  $x = 25 \text{ mm}$ , with a CO mole fraction increasing with  $x$  coordinate. The far-left part of both  $x$  profiles shows the CO consumption in the ERZ. The profile  $z = -48.5 \text{ mm}$  is chosen to compare the CRN performance against experimental data in the vicinity of the effusion cooling region. Until  $x = 27.5 \text{ mm}$  the amount of CO corresponds to the ERZ. After  $x = 27.5 \text{ mm}$ , the effusion cooling region starts. At the beginning of this zone there is a high value of CO concentration coming from the jet flow with high CO content, that reacts with the additional air entering this area and lowers its CO concentration. It rises again because of the flow entrained in the second near-effusion reactor, since more flow containing CO and fuel is entrained in this part of the system. The mole fraction decrease is slower than before: the trend is correctly caught by the CRN near-wall reactor, although the exact value is not reproduced. This zone is followed by a last exit-region near-wall PFR: although the temperature is far lower than the average combustor temperature, the CO concentration decreases fast due to mixing and further reaction, reaching the lowest measured value (in the order of  $\sim 10 \text{ ppm}$ ). This is attributed to the entrainment of completely reacted flow pockets and continuous mixing with the effusion air entering the system along its length. The vertical profile  $x = 175 \text{ mm}$  compares

the results on a vertical line almost at the exit of the combustion chamber, where average values are correctly reproduced.

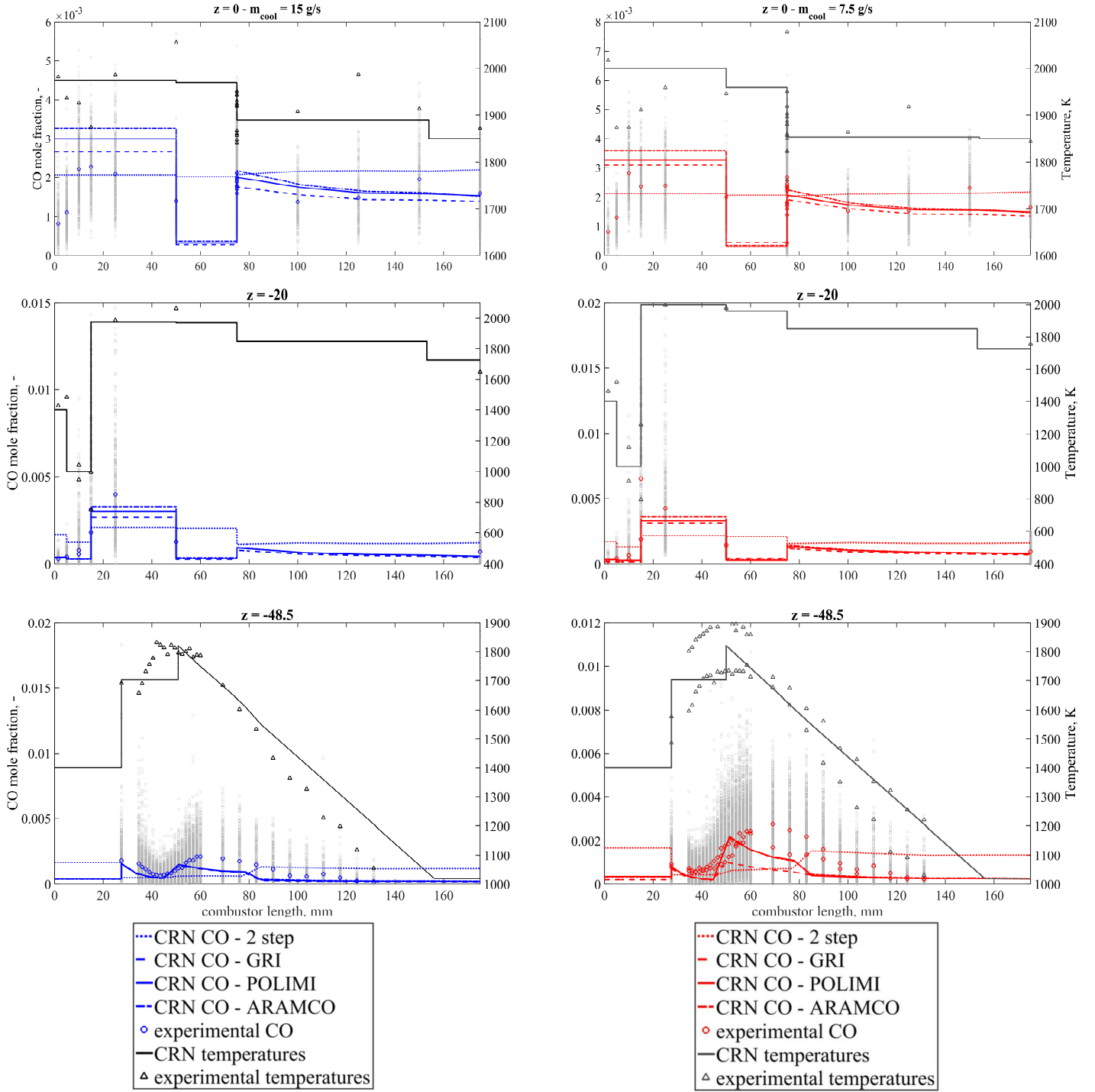


Figure 41: comparison between experimental data and CRN-predicted CO concentration values along horizontal profiles,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Several kinetic mechanisms are applied. The grey circles are experimental CO single-shot concentration values.



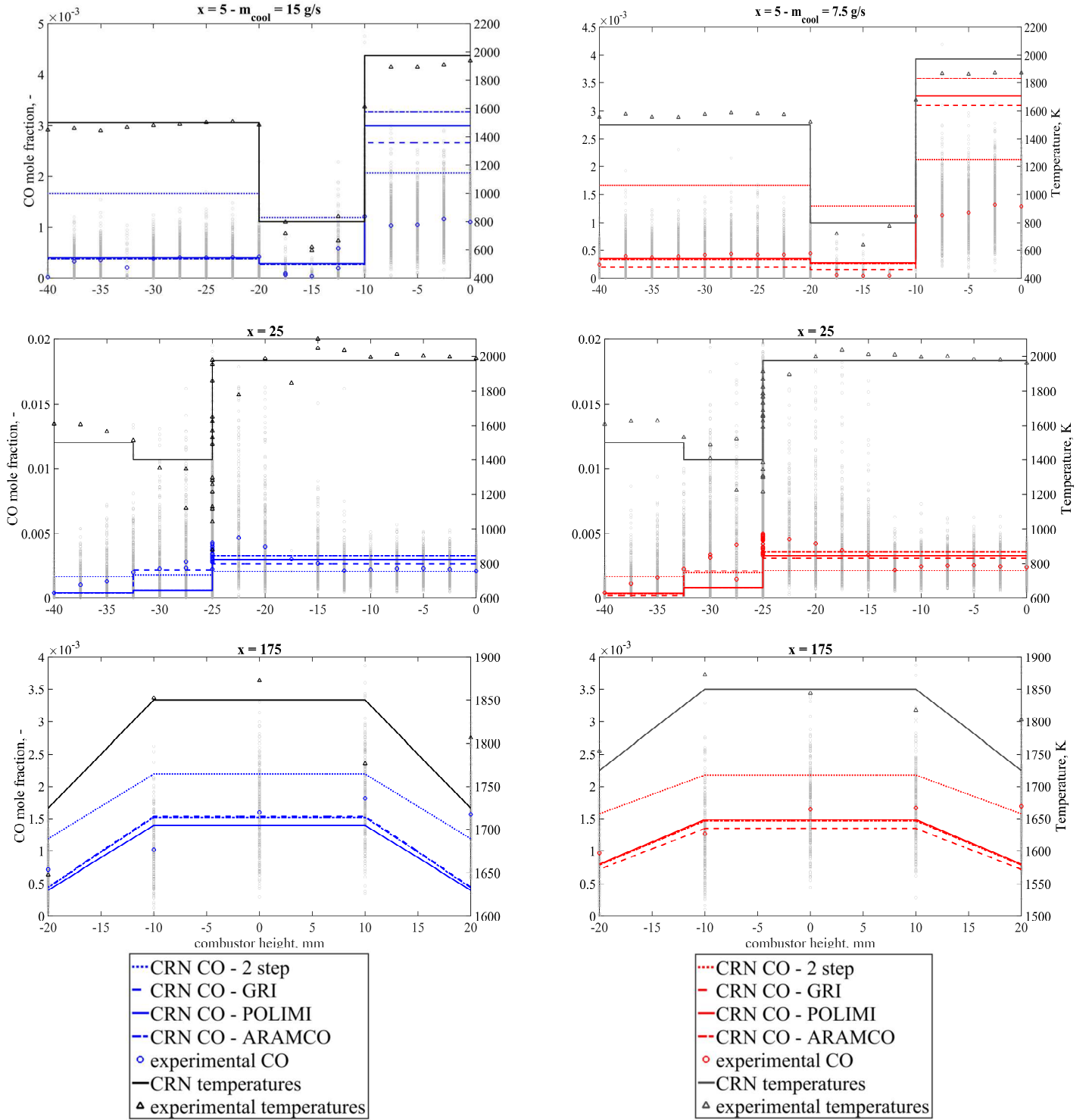


Figure 42: comparison between experimental data and CRN-predicted CO concentration values along vertical profiles,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Several kinetic mechanisms are applied. The grey circles are experimental CO single-shot concentration values.

As shown in the comparison carried out, the CRN model reproduces the CO evolution trends throughout the combustor with reasonable agreement along several selected profiles. In certain areas inside the combustion chamber the measured values of CO concentration are not exactly reproduced. One of the critical areas is the one identified as “flame zone” (see Figure 33 – Figure 36). According to the comparison in Figure 41,  $z = 0 \text{ mm}$ , the calculated mole fraction value is higher in the flame zone with respect to experiments. This slight discrepancy is attributed to the employment of a single macro-zone to outline this region, encouraged by previous works ([57], [59], [86], [123]). The consequence of this choice is a value of CO mole fraction that is average between the extreme values  $x$  measured this region:



0.004 in the flame region and 0.001 in the early IRZ, for  $m_{cool} = 15$  g/s. Despite an evident disagreement in some of the selected profiles, an average value between the limit measured values gives confidence about the validity of the schematization. Along the effusion cooling liner, the decreasing-increasing trend along the length of the combustor is correctly reproduced, although the exact value is not always caught. The discrepancy is attributed to the intense turbulent mixing present in the system, that is severely simplified in a coarse zonal model. Nonetheless, capturing the trends and the values in certain locations is an important result for a CRN employing macromixing zones, and confirms its adequacy to investigate the combustion process in the SSGT in different operating conditions. The CRN model is therefore employed in the following paragraphs to evaluate the influence of the different operating parameters on CO and other pollutants formation in the gas turbine model combustor under realistic boundary conditions.

### 3.4 Results and discussion

In this section, the results obtained from the CRN fit applied to the investigated operating conditions are shown and discussed. First, the isothermal flow fits are studied in terms of characteristic times and shapes of the global distributions. Each operating condition shown is compared to the standard operation point, which is summarized in Table 8.

Table 8: relevant boundary conditions of the standard operation point.

	Standard operation point, units	
Preheating temperature	623	K
System pressure, $P$	2.5	bar
Main air mass flow, $m_{in\_main}$	30	g/s
Equivalence ratio, $\phi_{lean\ premixed}$	0.75	[-]
Swirl number, $S$	0.7	[-]
Effusion cooling mass flow, $m_{cool}$	15	g/s
Fuel staging ratio, $st.$	0%,	[-]

The RTDs for the reactive measurements follow the section on the cold flow results. In this case, a discussion about the impact on the operating condition on the species formation in the SSGT accompanies the discussion about the global RTD quantities.

#### 3.4.1 Cold flow results

The impact of the boundary conditions on the RTD of the system is described. With respect to Table 8, the following variations on the parameters were explored.

Table 9: explored parameters for the cold-flow measurements.

	Operation point, units	
System pressure, $P$	2.5 and 3	bar
Swirl number, $S$	0.7 and 1.3	[-]
Effusion cooling mass flow, $m_{cool}$	15 and 7.5	g/s
Fuel staging ratio, $st.$	0% and 50%	[-]

The results are presented in the following order:

- effect of effusion cooling mass flow,  $m_{cool}$ ,
- effect of the fuel-staging ratio,  $st.$ ,
- effect of the operating pressure,  $P$ ,
- effect of the swirl number,  $S$ .

### 3.4.1.1 Effect of effusion cooling mass flow

The CRN-fit tracer responses are depicted in Figure 43. The main conclusion is already clear: a lower effusion cooling mass flow has a lower impact on the mixing field inside the combustion chamber. For  $m_{cool} = 15 \text{ g/s}$  there is a visible distinction between  $Out_1$  and  $Out_2$  (quantified in Table 10), as the latter shows an earlier rise. This feature is not visible for  $m_{cool} = 7.5 \text{ g/s}$ , where the distributions overlap. The impact of a lower amount of coolant flow for a given measurement position is shown on the lower row of Figure 43. Less cooling air delays the distribution, and this effect is clearer and more pronounced on  $Out_2$ , more sensitive to changes in the lower part of the combustor.

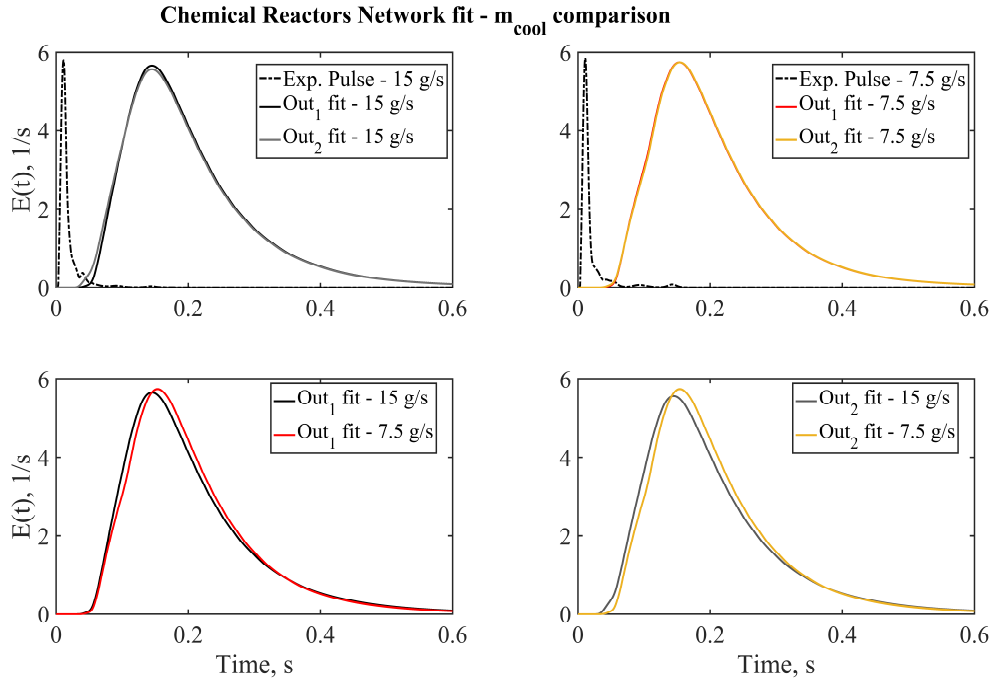


Figure 43: CRN-fit experimental tracer responses,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Upper row:  $Out_1$  and  $Out_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

Figure 44 shows the extracted RTDs. For the two operating conditions under investigation, which are also the reference ones as explained in paragraph 3.2.2, the comparison is carried out showing the RTDs relative to both measurements locations as well. They show several huge peaks, out of scale with respect to the mean of the distributions, which are associated with the entrainment of the tracer in the effusion cooling region.

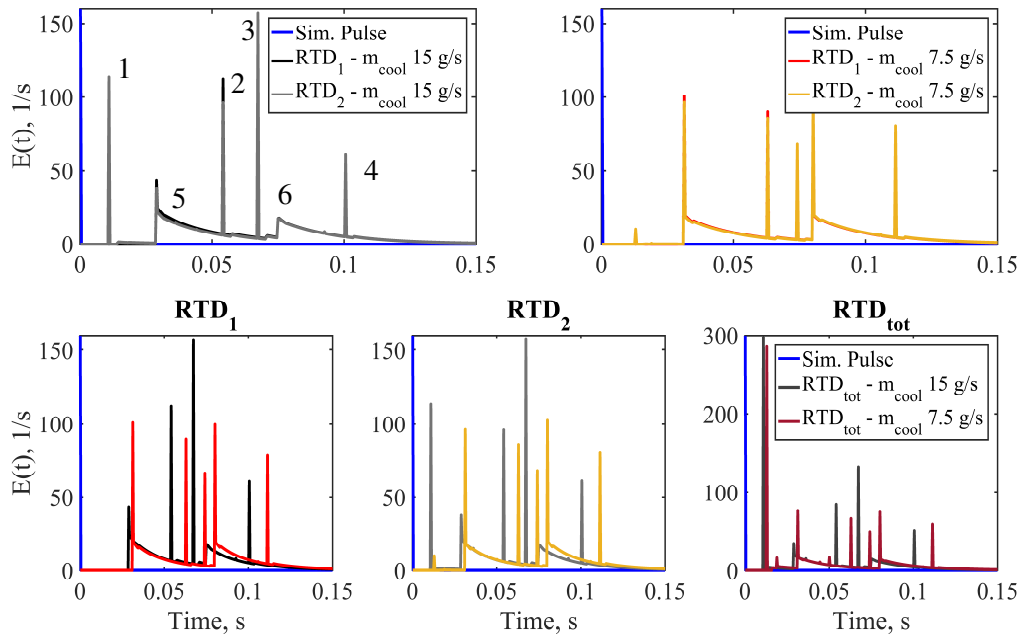


Figure 44: RTDs extracted from the calibrated CRN,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Upper row:  $Out_1$  and  $Out_2$  for the two investigated operating conditions; lower row: comparison between different operating conditions for the same measurement location.

Multiple peaks are present, exemplifying the different entrainment opportunities in the PFR-zones. The association between a phenomenon and a given peak is based on the analysis of the residence times in each zone. This value is one of the outputs of a model whose parameters have been optimized against the response of the system. The following features are distinguished:

- immediate entrainment in the effusion cooling region (peak “1”, Figure 44),
- first entrainment in the effusion cooling region and later mixing in the main flow (“2”, “3” and “4”, Figure 44).

These flow paths are better explained in Figure 45. In this figure, the identified pathways have been sketched and linked to the peaks shown in Figure 44.

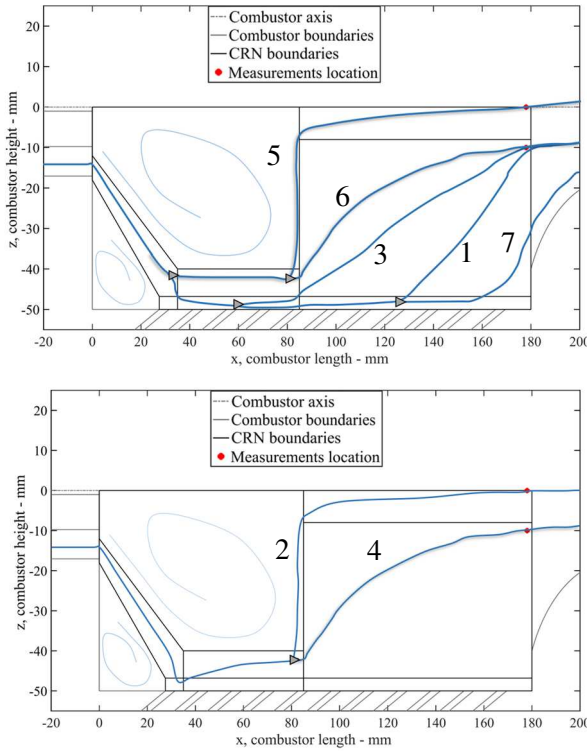


Figure 45: basic sketch of the identified flow paths responsible for the appearance of the ensemble of peaks differently delayed with respect to each other. A grey triangle symbolizes a splitting element, in accordance with the CRN legend, introduced in Figure 23 and Figure 33. The lighter curves indicate the position of the RZs. Besides the paths found in Figure 44 and described here, another path, number 7, is possible: part of the flow is entrained in the effusion cooling region and exits undetected. This part of the flow is accounted for only in the  $RTD_{tot}$ .

Instead, the local maxima at  $t \sim 0.03$  s and  $t \sim 0.07$  s, “5” and “6”, are attributed to the portion of tracer that follows the main flow paths. These two peaks show an exponential decay after a sharp rise by virtue of the parallel mixing in the recirculation zones. More specifically, “5” represents the portion of the flow following the jet-like region and then mixing in the central PFR at the exit. The peak “6” represents the portion of the flow that mixes in the side PFR after passing the jet region. From the coupled analysis of Figure 44 and Figure 45 emerges that the flow entrained from the main path in the cooling path reaches the exit later than the flow entrained in the lower path right at the beginning of the effusion cooling liner, peaks “2” and “3”.

The bypass-effect of the effusion path is nonetheless present in  $m_{cool} = 7.5$  g/s as well, as evident from Figure 44. However, its contribution to  $RTD_2$  with respect to  $RTD_1$  is negligible, especially if compared to  $m_{cool} = 15$  g/s: it was indeed not possible to discern it by judging the tracer responses alone. This is confirmed by the  $\tau_i^c$  values reported in Table 10. Here, the parameter  $\frac{m_{cooling-main}}{m_{total\_feed}}$  is reported, as an attempt to quantify the involvement of the near-wall path on the global mixing characteristics. As reported, its value is approximately half while feeding half the effusion cooling mass flow.

Besides the clear differences attributed to the main flow-effusion cooling interaction, the RTDs present a similar behaviour, exemplified by the global moments of the three distributions, Table 10. The parameters shown in Table 10, and in the other comparison tables, are explained in Table 5. The  $\tau_i^m$  are similar, slightly higher in the case of  $m_{cool} = 7.5$  g/s because of the lower flow rate introduced in the system. The  $\tau_i^{0.95}$  and  $\tau_i^{0.99}$  highlight the same tendency, as well as the higher moments of the distributions. It is interesting to notice the time range between these two characteristic times: 95% of the tracer gets outside of the system before 0.2 s, while additional 0.3 s, and thus more than 2 times the  $\tau_i^{0.95}$ , are required to reach the point where 99% has left the system. This phenomenon is attributed to the continuous entrainment in the recirculation zones, indicated in Table 10 as  $\frac{m_{IRZ}}{m_{in\_main}}$  and  $\frac{m_{ERZ}}{m_{in\_main}}$ : a great amount of flow is entrained and recirculated, especially in the IRZ.

Table 10: global properties of the RTDs and CRN-fit parameters,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ .

	$m_{cool}$ $= 15 \text{ g/s}$	$m_{cool}$ $= 7.5 \text{ g/s}$		$m_{cool}$ $= 15 \text{ g/s}$	$m_{cool}$ $= 7.5 \text{ g/s}$
$\tau_1^m$	0.081	0.089	$\tau_1^c$	0.029	0.031
$\tau_2^m$	0.080	0.090	$\tau_2^c$	0.011	0.013
$\tau_{tot}^m$	0.072	0.077	$\tau_{tot}^c$	0.011	0.013
$\sigma_1^2$	0.0054	0.0054	$\tau_1^{0.95}$	0.16	0.18
$\sigma_2^2$	0.0055	0.0054	$\tau_2^{0.95}$	0.16	0.18
$\sigma_{tot}^2$	0.0057	0.0058	$\tau_{tot}^{0.95}$	0.16	0.17
$S_1^3$	5	5	$\tau_1^{0.99}$	0.443	0.446
$S_2^3$	5	5	$\tau_2^{0.99}$	0.441	0.447
$S_{tot}^3$	5	4	$\tau_{tot}^{0.99}$	0.43	0.43
$\tau_{IRZ}$	0.011	0.012	$m_{cooling \rightarrow main}$	0.30	0.14
$\tau_{ERZ}$	0.17	0.17	$m_{total\_feed}$		
$m_{IRZ}$	1.3	1.2	$m_{main \rightarrow cooling}$	0.27	0.32
$m_{in\_main}$			$m_{total\_feed}$		
			$m_{ERZ}$	0.08	0.08
			$m_{in\_main}$		

### 3.4.1.2 Effect of fuel staging

To properly describe the flow phenomena while altering a certain amount of fuel staging, a slight modification of the network was necessary to consider the extra feed-stream and the different mixing phenomena it might induce. Referring to Figure 23 and Figure 24 for the basic CRN (no fuel staging), the modified near-nozzle region is shown in Figure 46. It follows the model proposed by [81], adopted and adjusted by [80], [106]. The model in Figure 46 has one more mixed zone that receives flow from the pilot tube, and entrains flow emerging from the plenum and from the IRZ: in this way, the main features linked to the presence of an additional flow are addressed. The flow from this pilot zone is then entirely entrained into the IRZ.

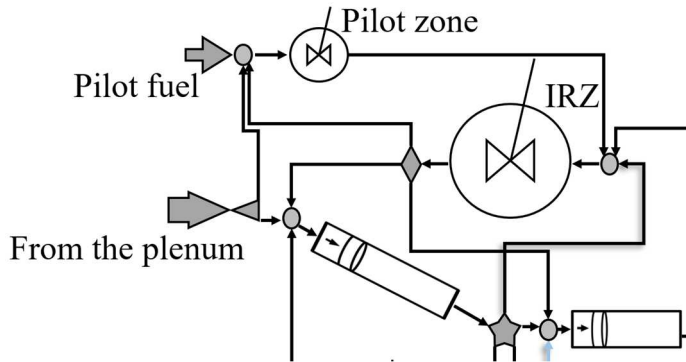


Figure 46: modified network to describe the near-nozzle region for fuel-staging operation. A CSTR reactor to exemplify the injection of the pilot-fuel has been added in the IRZ.

The CRN-fits for the case without fuel staging,  $st. = 0\%$ , and for the case with 50% fuel staging,  $st. = 50\%$ , are displayed in Figure 47. In these cases, as  $m_{cool}$  was kept constant, the behaviors of the tracer responses with respect to different measurement locations are similar:  $Out_2$  shows the exit of tracer earlier than the higher measurement location. As found in section 3.4.1.1, the near-effusion liner zone acts as a bypass zone, although this effect is less pronounced in this case.

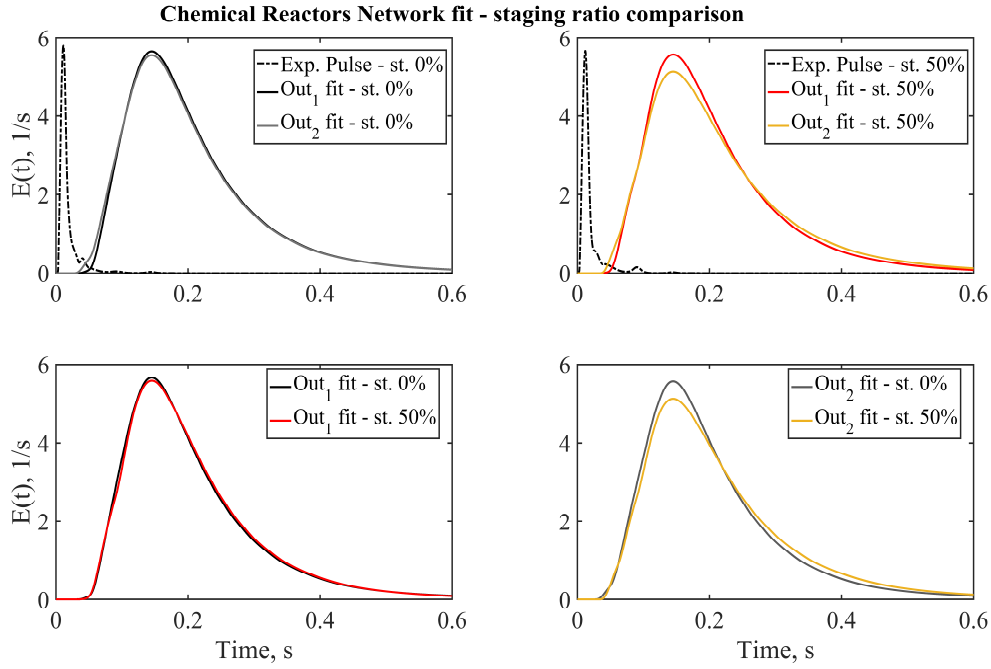


Figure 47: CRN-fit experimental tracer responses. Upper row:  $Out_1$  and  $Out_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

RTDs are illustrated in Figure 48. Although the bypass-feature of the effusion cooling is evident for  $st. = 50\%$  from peak “3”, it appears delayed with respect to the same feature in  $st. = 0\%$ . As indicated by  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ , reported in Table 11, there is a lower amount of mass flow involved in the mixing with cooling air.

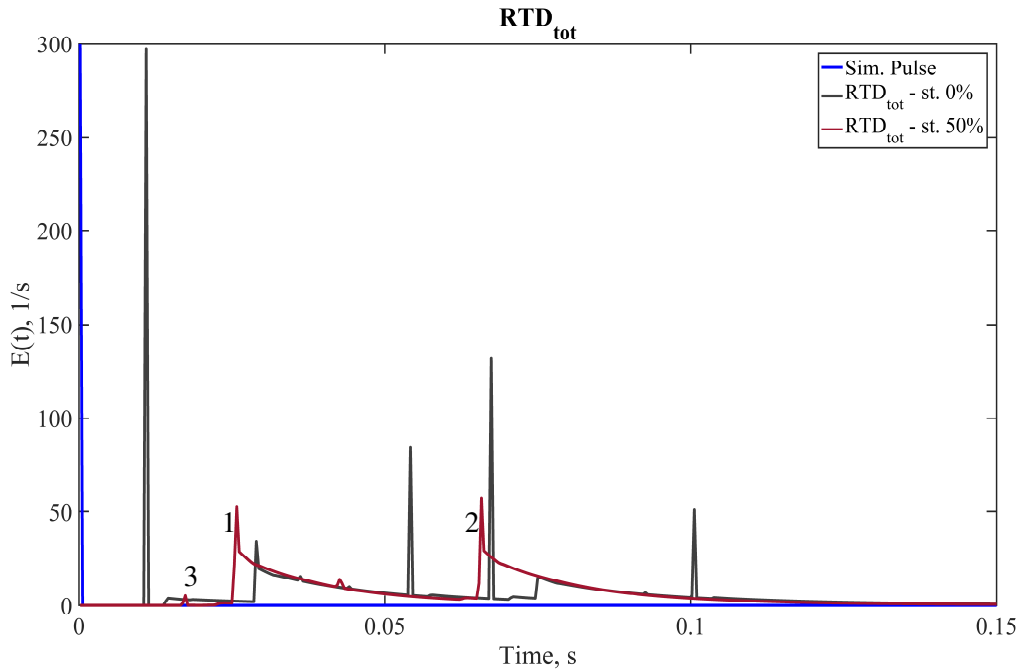


Figure 48: Global RTD of the combustion chamber  $st. = 0\%$  and  $st. = 50\%$ .

This is attributed to the presence of an additional mixing volume (Figure 46) that entrains flow and alters the mixing time in the IRZ. The first direct effect of this additional volume is a reduction of the IRZ-size. Furthermore, it causes a higher share of mass flow to mix in this region, presumably due to additional entrainment by the Pilot zone: more mass flow is entrained in the IRZ ( $\frac{m_{IRZ}}{m_{in\_main}}$ ), and less is

available to take the effusion path. The entrainment in the ERZ is also enhanced,  $\frac{m_{ERZ}}{m_{in\_main}}$ . The seeding passing through the jet regions and then entrained in the central exit zone, “1” in Figure 48, exits the combustion chamber earlier for  $st. = 50\%$  compared to the absence of pilot fuel. Two factors are identified to explain this phenomenon. The first has been addressed before and concerns the higher amount of mass flow available in the main flow, inducing lower characteristic times. In addition to that, there is direct entrainment of tracer in the IRZ via the Pilot zone CSTR (Figure 46), and therefore, a certain amount of tracer available for mixing before the delay time induced by the jet region. The two maxima, “1” and “2”, are associated to the passing time necessary to complete one of the two available PFR flow paths: the centerline or the lateral zone. The rearrangement of the flow caused by the presence of the pilot-fuel region generates a distribution with a longer  $\tau_{tot}^m$ , attributed to a reduced residence time and lower overall mass flow in the cooling region. Instead,  $\sigma_{tot}^2$  is lower, due to the reduced residence time in each recirculation zone. The same conclusion can be drawn by looking at the  $\tau_{tot}^{0.95}$  and  $\tau_{tot}^{0.99}$ :  $\tau_{tot}^{0.95}$  is longer for  $st. = 50\%$ , as an effect of the higher share of mass flow recirculated and the influence of a lower mass flow in the effusion path. However,  $\tau_{tot}^{0.99}$  is shorter for staged operation, because a higher recirculated mass flow reduces the residence time as well.

Table 11: global properties of the RTDs and CRN-fit parameters

	$st. = 0\%$ :	$st. = 50\%$ :		$st. = 0\%$ :	$st. = 50\%$ :
$\tau_{tot}^m$	0.072	0.074	$\tau_{tot}^c$	0.0286	0.0250
$\sigma_{tot}^2$	0.0057	0.0042	$\tau_{tot}^{0.95}$	0.16	0.17
$S_{tot}^3$	5	5	$\tau_{tot}^{0.99}$	0.44	0.38
$\tau_{IRZ}$	0.011	0.009	$m_{IRZ}/m_{in\_main}$	1.3	1.7
$\tau_{ERZ}$	0.17	0.12	$m_{ERZ}/m_{in\_main}$	0.08	0.12
$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	0.30	0.29	$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	0.27	0.01

### 3.4.1.3 Effect of operating pressure

The tracer responses obtained by fitting the cold flow CRN to the RTD measured at increased pressure is shown in Figure 49. What clearly emerges is the almost perfect overlap of the two distributions measured at different positions at  $P = 3$  bar.

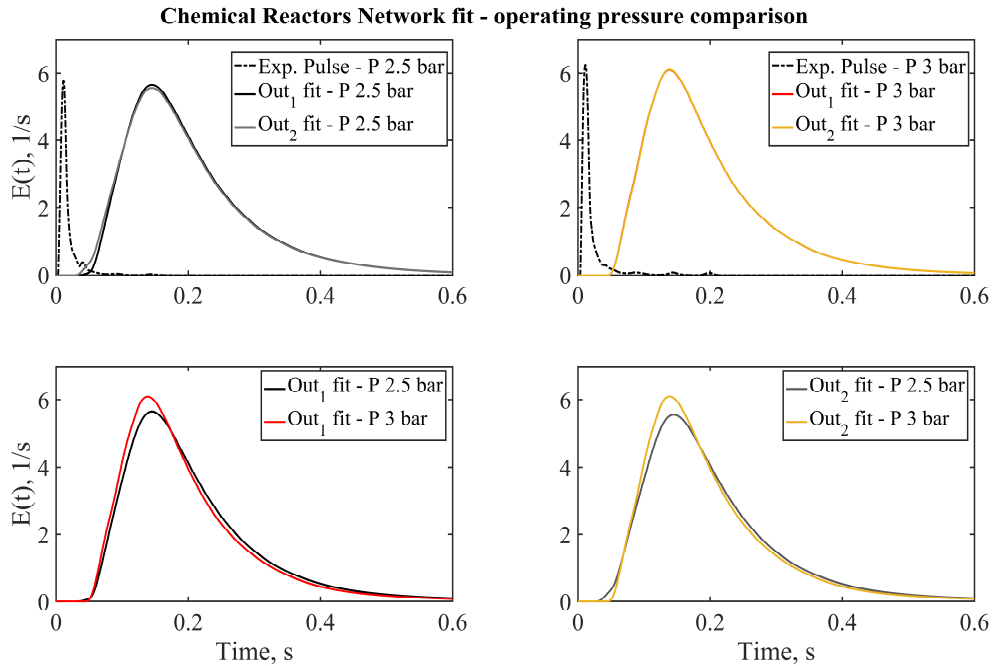


Figure 49: CRN-fit experimental tracer responses. Upper row: Out<sub>1</sub> and Out<sub>2</sub> for  $P = 2.5$  bar and  $P = 3$  bar ; lower row: comparison between the same measurement location for different operating conditions.

In Figure 50 the global exit RTD for the two operating conditions with different pressure are compared, while RTD-based parameters are calculated and compared in Table 12. The explanation to the spatially coupled evolution of the tracer concentration over time, shown in Figure 49 and evident also by the lack of sharp peak preceding the whole RTD in Figure 50, experienced by both probing locations, lies in the altered interaction with the cooling region as the pressure increases. The amount of mass flow from the cooling area to the main area (expressed by  $\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$ ) is approximately the same for both investigated operating condition. However, a drastic decrease (one order of magnitude) is experienced by the reverse flow, as evident from  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ . The lack of flow entrained in the effusion cooling region from the main flow is responsible for the increased passing times in the lower path, making them comparable to those of the main path. Referring to Figure 50, “1” denotes the time of arrival of the tracer from the centreline path, followed by the rest of the tracer in “2”, where the flow in the outer region reaches the exit. Because of the already mentioned dramatically decreased mixing from the main flow to the effusion cooling flow, the contribution from the amount of flow entrained in the lower path to the global RTD is negligible, and barely distinguishable in form of negligible peaks in the global distribution. An exception is presented by “3”. Its time of appearance corresponds to entrainment of the tracer in the effusion cooling flow from the beginning of the effusion cooling liner. As pointed out in paragraph 3.4.1.1, the flow that experiences mixing with cooling air from the beginning of the liner takes a longer time to pass through the combustor (refer to the lower image in Figure 45).

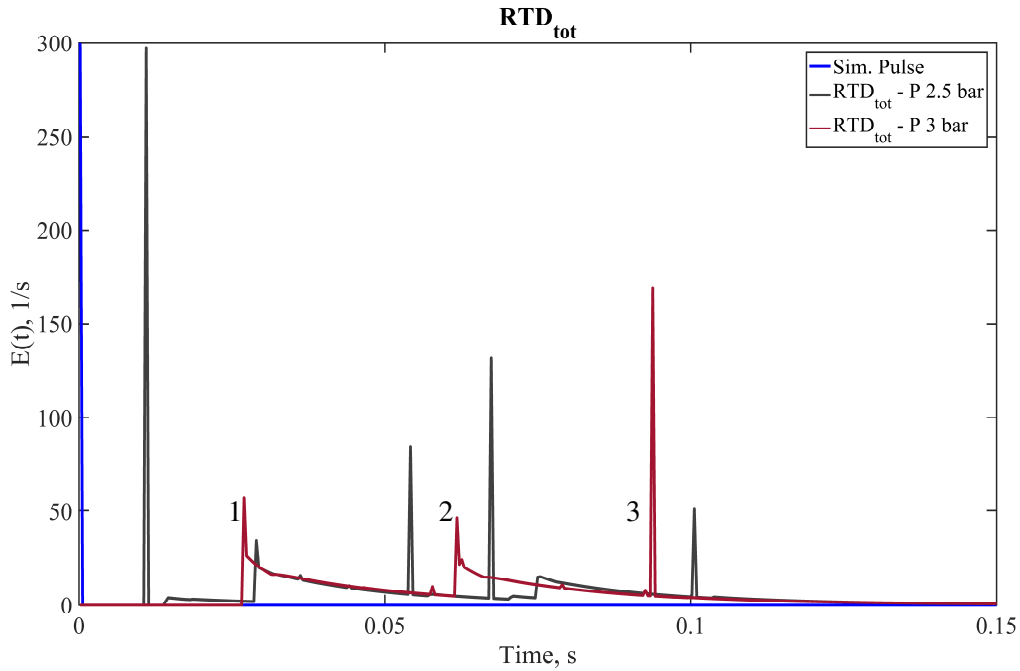


Figure 50: Global RTD of the combustion chamber  $P = 2.5$  bar and  $P = 3$  bar.

The distribution calculated for  $P = 3$  bar exhibits a longer mean residence time, but both  $\tau_{tot}^{0.95}$  and  $\tau_{tot}^{0.99}$  take similar values, Table 12. More mass flow is entrained in both RZs, by virtue of the lower momentum of the flow caused by the higher pressure, and the residence times in those zones are therefore lower.



Table 12: global properties of the RTDs and CRN-fit parameters,  $P = 2.5$  bar and  $P = 3$  bar

	$P = 2.5$ bar	$P = 3$ bar		$P = 2.5$ bar	$P = 3$ bar
$\tau_{tot}^m$	0.072	0.082	$\tau_{tot}^c$	0.011	0.027
$\sigma_{tot}^2$	0.0057	0.0056	$\tau_{tot}^{0.95}$	0.16	0.19
$S_{tot}^3$	5	5	$\tau_{tot}^{0.99}$	0.43	0.44
$\tau_{ERZ}$	0.17	0.14	$m_{IRZ}$	1.3	1.9
			$m_{in\_main}$		
$\tau_{IRZ}$	0.011	0.008	$m_{ERZ}$	0.08	0.12
			$m_{in\_main}$		
$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	0.30	0.38	$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	0.27	0.06

#### 3.4.1.4 Effect of swirl number

In Figure 51 the tracer responses that result from the CRN-fitting of the data for  $S = 0.7$  and  $S = 1.3$  are presented. The shape of the distribution curves gets broader and exhibits a lower value of the maximum going from  $S = 0.7$  to  $S = 1.3$ , by virtue of the higher amount of recirculated mass flow. The accelerating effect of the lower path in the combustor is evident in Figure 51 also for a higher value of  $S$ . The effect of an increased swirl number on the global flow characteristics can be described comparing the  $Out_1$ - measurement position of both operating conditions: the rising edge of  $Out_1$  generated with  $S = 1.3$  is delayed with respect to  $Out_1$  for  $S = 0.7$  (more evident for the RTD in Figure 52). In the former case, the tangential momentum flux is increased and the axial momentum flux lower, slightly delaying the appearance of the seeding at the centreline probing location. At the lower location, however, two effects result in an earlier appearance of tracer: higher mass flow pushed towards the boundaries following the swirl motion (as quantified by an additional parameter considered in this case, the ratio  $\frac{m_{outer\_region\ S=1.3}}{m_{outer\_region\ S=0.7}}$ , Table 13) and subsequent entrainment in the effusion cooling region.

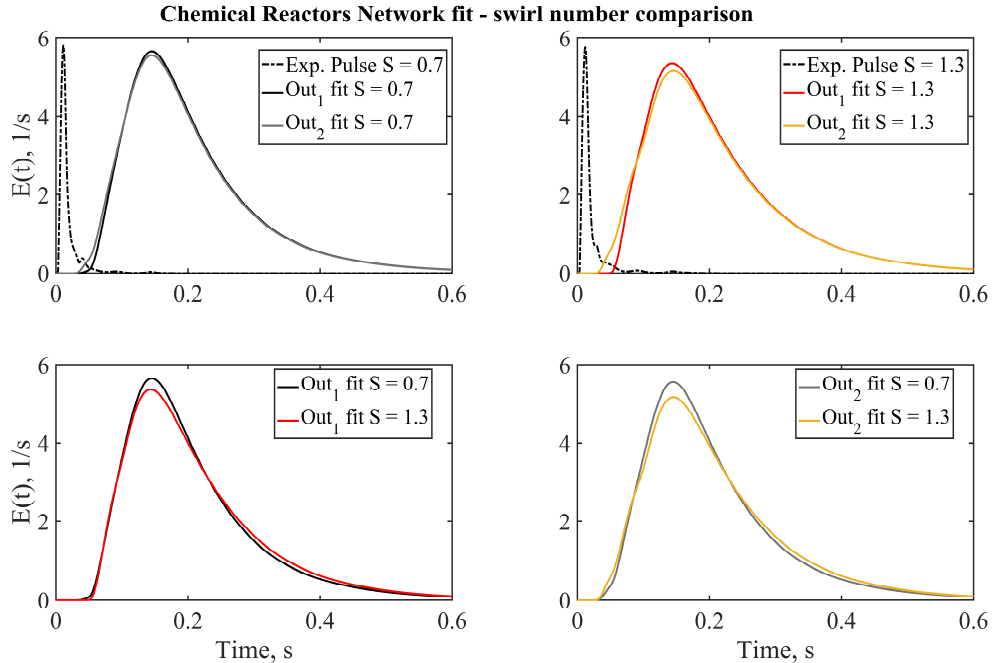


Figure 51: CRN-fit experimental tracer responses. Upper row:  $Out_1$  and  $Out_2$  for  $S = 0.7$  and  $S = 1.3$  the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

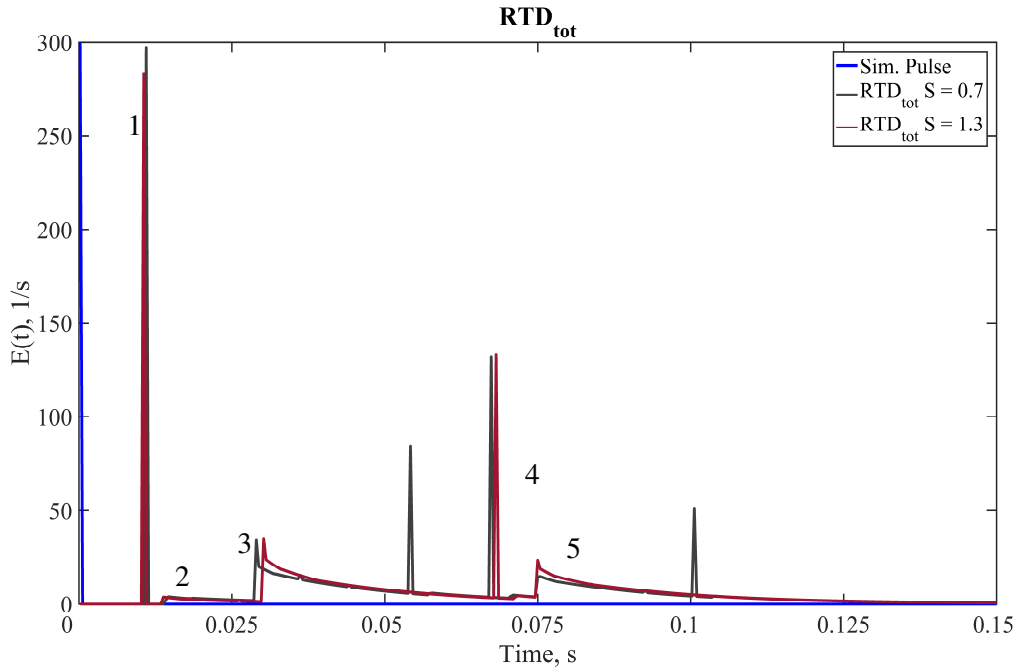
In Figure 52 the global exit RTD for the two operating conditions with different  $S$  are compared, while RTD-based parameters are given and compared in Table 13.

Table 13: global properties of the RTDs and CRN-fit parameters – swirl number ( $S$ ) variation

	$S = 0.7$	$S = 1.3$		$S = 0.7$	$S = 1.3$
$\tau_{tot}^m$	0.072	0.072	$\tau_{tot}^c$	0.011	0.010
$\sigma_{tot}^2$	0.0057	0.0045	$\tau_{tot}^{0.95}$	0.16	0.16
$S_{tot}^3$	5	4	$\tau_{tot}^{0.99}$	0.43	0.38
$\tau_{ERZ}$	0.17	0.13	$m_{cooling \rightarrow main}/m_{total\_feed}$	0.30	0.38
$\tau_{IRZ}$	0.011	0.010	$m_{main \rightarrow cooling}/m_{total\_feed}$	0.27	0.20
$m_{IRZ}/m_{in\_main}$	1.3	1.5	$\frac{m_{outer\_region\ S=1.3}}{m_{outer\_region\ S=0.7}}$	1.1	
$m_{ERZ}/m_{in\_main}$	0.08	0.10			

Identical to the standard operating condition, there is a first peak associated with entrainment in the effusion cooling path and immediate transport to the exit of the combustion chamber, “1”. Subsequently, “2” contains the flow recirculated in the recirculation zone and additionally in the effusion cooling region. Afterward, “3”, the flow following the main path reaches the outlet plane and exhibits the CSTR-decay to the catch-up of the flow trapped in the RZs. The peak “4” corresponds to the tracer first entrained by the cooling air and entrained by the main flow once again, as shown in the path number 3 in Figure 45. Instead, “5” corresponds to the path 6 in Figure 45: part of the flow following the jet region and exiting through the side segregated PFR.

As expected, the amount of recirculated mass flow is higher for a higher swirl number, both in the ERZ and in the IRZ. The higher share of recirculated flow causes a lower mean residence time in both recirculated zones. In the ERZ, a higher flow rate is accompanied by a reduction of the volume, because of a higher aperture angle of the flow issuing from the inlet nozzle. Concerning the IRZ, the higher angle increases the volume of the zone; nonetheless, this increase in the zone volume does not compensate the higher mass flow passing in the zone, and the residence time is therefore smaller with respect to  $S = 0.7$ . The interaction between main flow and cooling flow changes: there is more mass flow entrained from the effusion path, and less entrained in the lower path from the main flow region.

Figure 52: Global RTD of the combustion chamber,  $S = 0.7$  and  $S = 1.3$ .

### 3.4.1.5 Summary

In this chapter, the impact of the operating conditions on the RTD of the SSGT under non/reactive conditions has been described referring to the standard operation point. In Table 14, some relevant parameters are given to provide a comparison among the investigated sets of boundary conditions. Beside the global mean residence time inside the combustor,  $\tau_{tot}^m$ ,  $\frac{m_{recirculation}}{m_{in\_main}}$  represents the total share of the flow entrained in the recirculation regions and  $\frac{m_{main\_cooling}}{m_{total\_feed}}$  calculates the ratio of the total mass flow exchanged between the two flow paths (main and cooling) with respect to total mass flow fed to the system.

Table 14: comparison among the different investigated operating points.

	Basic operating point (Table 8)	$m_{cool}$ = 7.5 g/s	st. = 50%	P = 3 bar	S = 1.3
$\tau_{tot}^m$	0.072	0.077	0.074	0.082	0.072
$\frac{m_{main\_cooling}}{m_{total\_feed}}$	0.57	0.38	0.30	0.44	0.58
$\frac{m_{recirculation}}{m_{in\_main}}$	1.4	1.3	1.8	2.0	1.6

From Table 14 it can be concluded that that a lower cooling mass flow yields a higher global mean residence time in the combustor, presumably linked to the lower mass flow in the system. The overall mixing between the two identified paths is lower, and the entrainment in the RZs is approximately the same order of magnitude as operating with a higher cooling mass flow.

The presence of a pilot-flow has a slight increasing effect on  $\tau_{tot}^m$  and clearly alters the mixing behaviour of the system increasing the entrainment in the recirculation zones. The interaction between the main and cooling paths in terms of exchanged mass flow appears lowered.

A higher P greatly enhances the mixing in the recirculation zones, presumably because of the lower momentum of the flow. The slower evolution of the distribution is also attributed to the pressure increase. The global amount of mass flow exchanged between the main paths is decreased.

Finally, a higher swirling ratio S does not affect the mean residence time in the system, but does increase the entrainment in the RZs, that is higher. Overall, the mixing between near-wall region and central region has the same value.

## 3.4.2 Reactive flow results

The impact of the boundary conditions on the system RTD during combustion is described. With respect to table 8, the following variation on the parameters were explored:

Table 15: explored parameters for the reactive-flow measurements.

	Operation point, units	
System pressure, $P$	2.5 and 3	bar
Swirl number, $S$	0.7 and 1.3	[-]
Effusion cooling mass flow, $m_{cool}$	15 and 7.5	g/s
Fuel staging ratio, st.	0%, 10%, 30% and 50%	[-]
Equivalence ratio, $\phi$	0.65, 0.75 and 0.85	[-]

Beside the description of the RTDs, aided by the discussion of selected network-derived parameters (explained in Table 5), the impact of the operating conditions on species production is also shown and discussed along selected profiles, shown in the schematic in Figure 53.

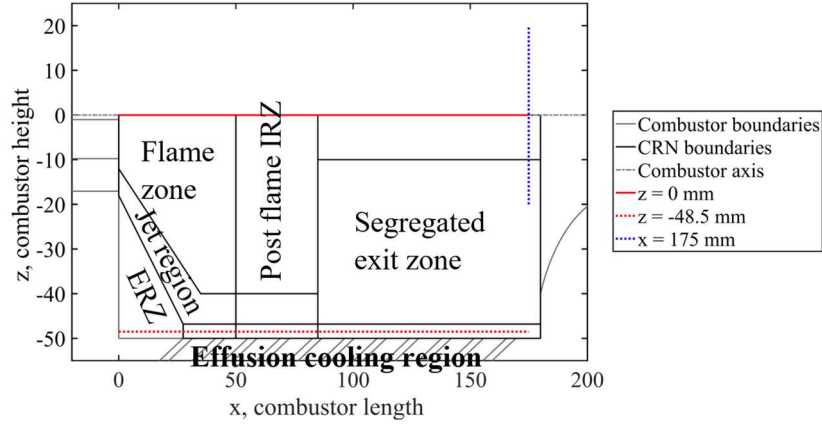


Figure 53: sketch of the lower half of the flame tube, with superimposed CRN boundaries. Radial (blue) and axial (red) location used to show species formation under different operating conditions are highlighted.

Following the interest on pollutant formation in gas turbine combustion, the following species were selected for comparison: CO, C<sub>2</sub>H<sub>2</sub> and NO<sub>x</sub>, the latter considered as the sum of the concentration of NO, N<sub>2</sub>O and NO<sub>2</sub>. Beside the polluting aspect of the listed species, CO and C<sub>2</sub>H<sub>2</sub> are directly linked to the incomplete combustion of the fuel, addressing the need for combustion device optimization. C<sub>2</sub>H<sub>2</sub> is also a soot precursor. As specified before, while dealing with CSTRs (flame, IRZ and ERZ) only one concentration value is displayed, namely the one referring to the concentration at the exit (see 2.1.1). A PFR shows instead a continuous evolution of the concentration along its axial coordinate, that serves also as a reaction time.

The results are presented in the following order:

- effect of effusion cooling mass flow,  $m_{cool}$ ,
- effect of the fuel-staging ratio,  $st.$ ,
- effect of the operating pressure,  $P$ ,
- effect of the swirl number,  $S$ ,
- effect of the equivalence ratio,  $\varphi$ .

#### 3.4.2.1 Effect of effusion cooling mass flow

Figure 54 shows the comparison among the different tracer responses recorded at the exit of the combustor. The upper row of images shows the two responses for a given mass flow, while the lower row compares the results at the same measurement location for different amounts of effusion air. Figure 54 confirms the effect of a lower quantity of cooling air on the measured responses, though less clear than in the non-reactive case, presumably due to the higher velocities associated to thermal expansion through combustion inside the chamber. A lower amount of effusion air introduced in the system corresponds to tracer responses that almost overlap, whereas there is a clear difference while feeding a higher mass flow of cooling air.

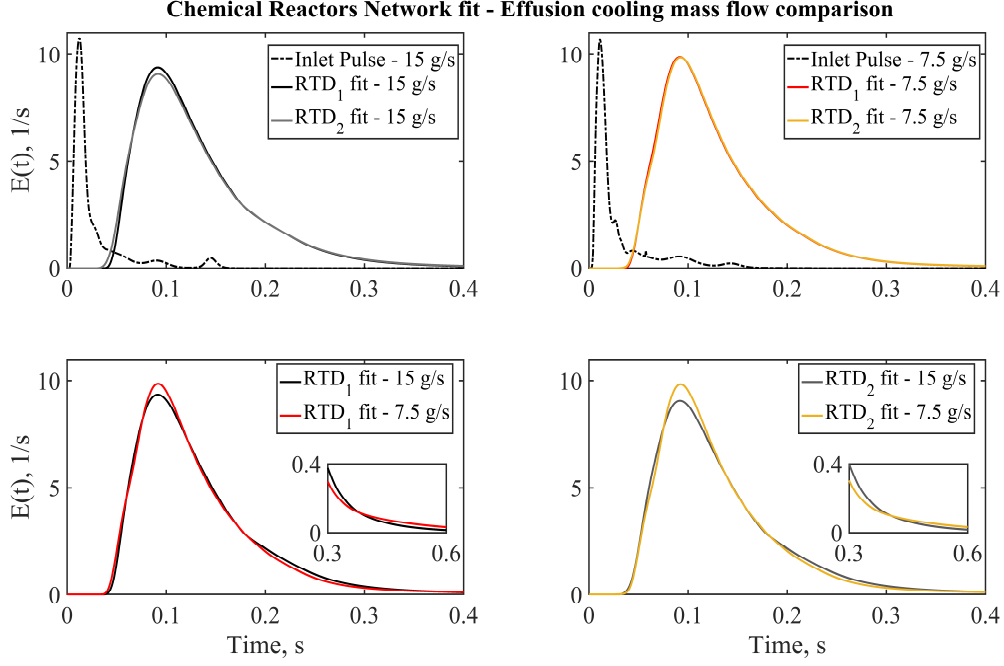


Figure 54: CRN-fit experimental tracer responses for  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Upper row:  $Out_1$  and  $Out_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

Figure 55, comparing the RTDs for both different measurements positions as well as the same measurement position for a different amount of cooling air, confirms the main phenomena already observed for the temporal evolution of the tracer: the impact of the cooling on the flow homogeneity is reduced for a lower amount of effusion cooling air introduced in the system.

Table 16: global properties of the RTDs and CRN-fit parameters,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ .

	$m_{cool}$ $= 15 \text{ g/s}$	$m_{cool}$ $= 7.5 \text{ g/s}$		$m_{cool}$ $= 15 \text{ g/s}$	$m_{cool}$ $= 7.5 \text{ g/s}$
$\tau_1^m$	0.026	0.032	$\tau_1^c$	0.010	0.012
$\tau_2^m$	0.026	0.032	$\tau_2^c$	0.001	0.012
$\tau_{tot}^m$	0.018	0.020	$\tau_{tot}^c$	0.001	0.001
$\sigma_1^2$	0.0013	0.0013	$\tau_1^{0.95}$	0.05	0.05
$\sigma_2^2$	0.0016	0.0013	$\tau_2^{0.95}$	0.05	0.05
$\sigma_{tot}^2$	0.001	0.001	$\tau_{tot}^{0.95}$	0.041	0.052
$S_1^3$	8	10	$\tau_1^{0.99}$	0.2	0.17
$S_2^3$	8	10	$\tau_2^{0.99}$	0.22	0.17
$S_{tot}^3$	10	12	$\tau_{tot}^{0.99}$	0.13	0.13
$\tau_{flame}$	0.0031	0.0028	$m_{IRZ}$	6.5	5
$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	0.43	0.49	$\frac{m_{in\_main}}{m_{ERZ}}$	0.15	0.16
$\tau_{ERZ}$	0.03	0.03	$m_{in\_main}$		
$\tau_{IRZ}$	5.8	8.0	$m_{flame}/m_{in\_main}$	0.97	1.00
$\times 10^{-4}$	$\times 10^{-4}$	$\times 10^{-4}$	$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	0.28	0.09

In more details, seeding is present at the exit of the combustor almost immediately ( $\sim 1 \text{ ms}$ , see Table 16) after the pulse input for  $m_{cool} = 15 \text{ g/s}$ . This portion of seeding is entrained in the flame zone, and then immediately in the near-cooling air region. Because of the flow rates involved, this part of the combustor can be regarded as a fast-bypass one, causing the fluid pockets entrained here to reach the

exit plane of the combustion chamber faster than the others. This holds true also for  $m_{cool} = 7.5 \text{ g/s}$  (see magnified area in Figure 55 and  $RTD_{tot}$ ). However, the flow entrained in the near wall path mainly continues towards the exit without significantly influencing the main flow, and it exits the combustor without being detected by either of the measurement location (except for the small amount, shown in the inset) and its presence is clear only looking at the  $RTD_{tot}$  (weighted mean of the RTDs obtained from the measured tracer response). This lower impact is also quantified in Table 16: the parameter  $\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$  is one order of magnitude lower for  $m_{cool} = 7.5 \text{ g/s}$ , confirming the lower involvement of the effusion cooling air in the global evolution of the main flow path. Mixing from the main path,  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ , shows instead the same order of magnitude, as it is not altered. Entrainment in the ERZ and in the flame zone is favoured for a lower amount of liner air introduced in the system, but entrainment in the IRZ is lower. Globally, the  $RTD_{tot}$  shows a higher  $\tau_{tot}^m$  for  $m_{cool} = 7.5 \text{ g/s}$ , in accordance to the lower global flowrate introduced in the system. The calculated  $\tau_{tot}^{0.99}$  is the same for both distributions, as it mostly depends on the mixing in the recirculation zones, which are not significantly altered by the reduction of the effusion cooling rate.

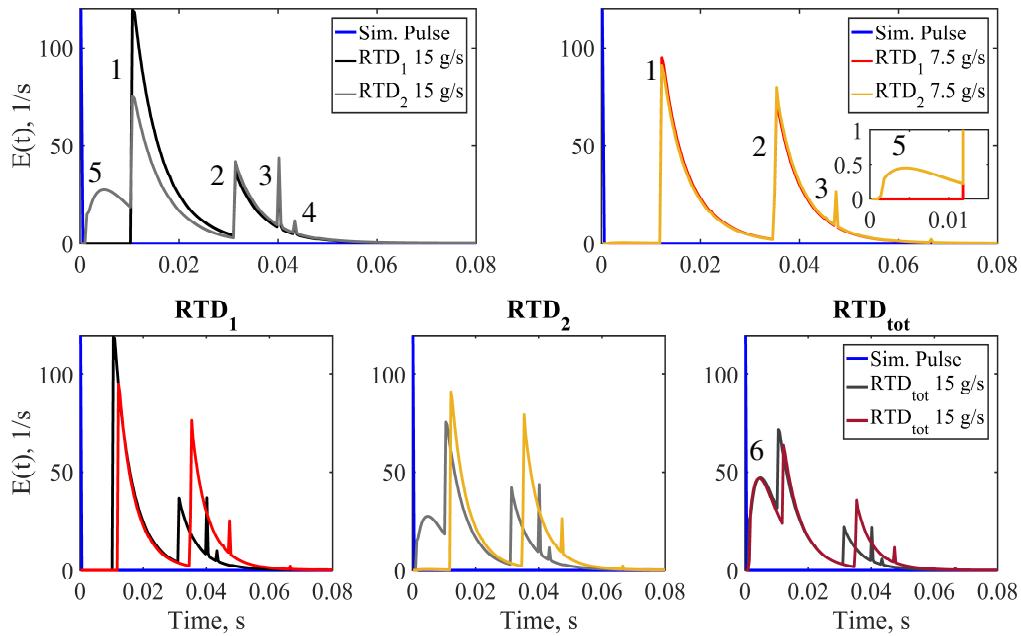


Figure 55: RTDs calculated from the CRN calibrated against the experimental tracer response,  $m_{cool} = 15 \text{ g/s}$  and  $m_{cool} = 7.5 \text{ g/s}$ . Upper row: comparison between  $RTD_1$  and  $RTD_2$  for the same value of the effusion cooling mass flow. Lower row: comparison between the  $RTD_i$  for different values of effusion cooling mass flow.

According to Figure 55, besides the initial part of the distribution, “5”, the identifiable peaks mainly stem from the mixing in the main flow path. Figure 56 helps the visualization of the possible flow paths by means of a basic sketch of the combustor and the possible routes. Each peak has been associated to a certain event based on the analysis of the residence time in each zone. After the initial mixing in the flame region, the flow entrained in the post-flame and central segregated-region PFR gives rise to the first peak, “1” in Figure 55. The portion of flow entrained in the post-flame and outer segregated-region PFR gives rise to the second one. The smaller, subsequent peaks derive from the exchange of flow between the main path and the effusion cooling path. Respectively, the third peak exemplifies the event of entrainment of flow from the main path at a later stage ( $\sim$  second or third near wall reactor), whereas “4”, comes from an earlier entrainment in the effusion region (already in the first liner-reactor).

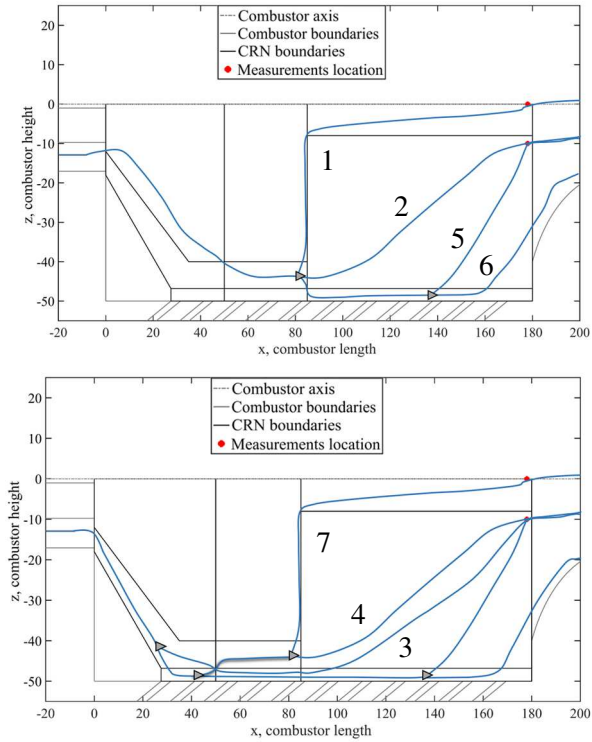


Figure 56: basic sketch of the identified flow paths for reactive flow. The grey triangle symbolizes a splitting element, in accordance with the CRN legend, introduced in Figure 23 and Figure 33. 6 represents the part of the flow that is not detected during the measurements and is accounted for in  $RTD_{tot}$  only. Additional numbers, like number 7, are added in the figure to highlight the different existing paths, that might acquire importance for different operating conditions.

Figure 57 reports on the influence of  $m_{cool}$  on species formation. As remarked in section 3.4.2, the following species were selected for comparison: CO,  $C_2H_2$  and  $NO_x$ .

The CO evolution along the centreline of the combustor ( $z = 0$ , Figure 57) presents only minor differences in the flame region.  $m_{cool} = 7.5 \text{ g/s}$  shows a higher in-flame CO production, in agreement with experimental data. This behaviour is attributed to both the slightly higher mass flow that is entrained into the flame zone from the main inlet stream for this boundary condition ( $m_{flame}/m_{in\_main}$ , Table 16) and to the higher temperature fit in this zone by the CRN optimization. These two factors point in the direction of a lower residence time in the flame zone, causing a lower conversion of CO. Along the effusion cooling liner ( $z = -48.5$ ) two CO formation peaks are identified, corresponding to the areas of higher flow exchange between the main path and the effusion cooling path (Figure 34). The operating condition of  $m_{cool} = 15 \text{ g/s}$  exhibits the highest CO concentration at the start of the cooling liner, because of the higher amount of reactive mixture entrained in this zone. The trend changes while looking at the second maximum in the CO concentration: higher CO levels are found for  $m_{cool} = 7.5 \text{ g/s}$ . In this case, the mixing features that characterize the two different operating conditions are strongly linked with this result: a higher  $m_{cool}$  entrains a higher quantity of reactive mixture from the surroundings, while being less prone to be entrained in the main flow. Therefore, the CO mole fraction is lowered by mixture that has already reacted in the previous near-wall reactor and by the higher mass flow entering the boundaries. On the other hand, for a lower  $m_{cool}$ , a higher share of the mixture exiting the first near-wall zone is entrained into the main path, and an overall lower mass flow is accessing the specific reactor. These differences soften until they disappear along the liner-zone, by virtue of the higher homogeneity reached in this zone from a mixing point of view and the almost complete CO conversion.

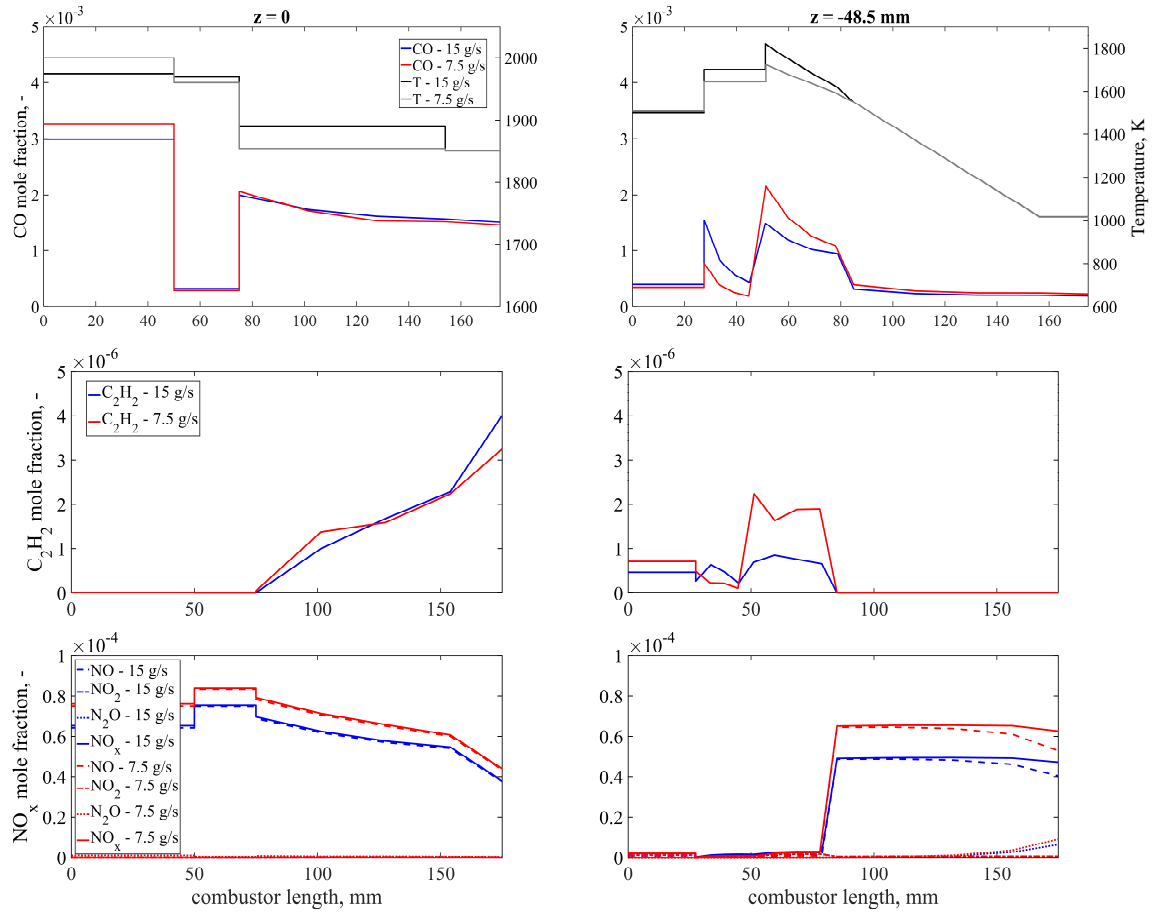


Figure 57: influence of  $m_{cool}$  on species formation. Upper row: CO along selected profiles, middle row:  $C_2H_2$ , lower row:  $NO_x$ .

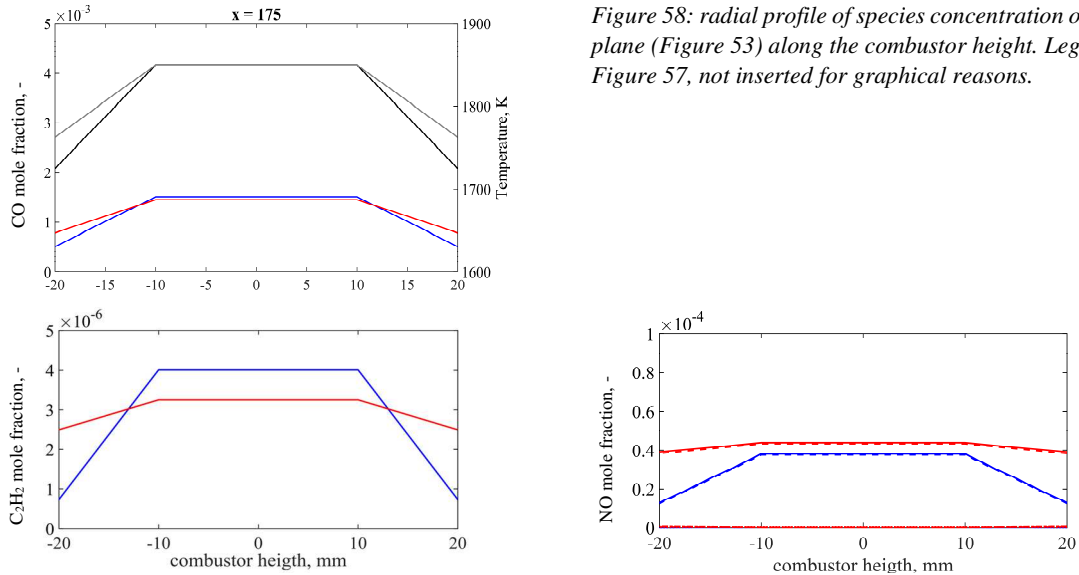


Figure 58: radial profile of species concentration on the exit plane (Figure 53) along the combustor height. Legend as in Figure 57, not inserted for graphical reasons.

Along the vertical profile at the exit of the combustor, Figure 58, shows a slightly higher CO concentration in the side reactor for  $m_{cool} = 7.5$  g/s, stemming from the lower mass flow rate passing in this region for this specific operating condition and the higher temperature of the side reactor. The second row in Figure 57 is dedicated to  $C_2H_2$ , whose overall amount is lower (three orders of magnitude or less) compared to CO. There is no acetylene in the flame and in the recirculation zone. Few ppm of the species are formed in the last PFR, because the small amount of fuel bypass reaching



this zone. Near the effusion cooling liner,  $C_2H_2$  shows the same trend as CO.  $C_2H_2$  is a dehydrogenated combustion intermediate, therefore, in an ideal situation, it should in the end be entirely converted into CO, that is then ideally completely converted to  $CO_2$ . Furthermore,  $C_2H_2$  reaction with OH radical plays a significant role in the CO formation, because of the following reaction path, Reaction 18, that involves  $C_2H_3 \cdot$  and  $C_2H \cdot$  as intermediates [25]:



The  $C_2H_2$  behaviour responds promptly to the arrival of partially reacted mixture, showing the maximum production in the second effusion cooling reactor. As commented before, partially reacted mixture reaches this point, and the further mixing with air at high temperature (though lower than flame temperature) encourages the formation of acetylene. Proceeding further along the liner, the species is no more produced, because the mixture here contains almost no fuel anymore, and the combustion reactions are basically done. In addition, mixing with flue gas coming from the main path further lowers its concentration. On the exit plane, the  $C_2H_2$  behaviour still closely resembles the one of CO.

The evolution of  $NO_x$  formation along the centreline shows, at first, that NO is the dominant species along the oxidized nitrogen products. It represents the most amount of nitrogen oxidized products, while  $NO_2$  and  $N_2O$  are present in much lower amount. The differences seen until the IRZ are attributable to both temperature effect and CO concentration: in the IRZ there is a low level of CO, therefore NO is not reduced again to  $N_2$  by CO. Instead, because of the additional time at high temperature, its concentration rises with respect to flame concentration. The NO concentration slowly decreases towards the exit, with a higher concentration for  $m_{cool} = 7.5 \text{ g/s}$ . Along the cooling liner, the  $NO_x$  mole fraction is in the sub-ppm region until approximately half of the combustor length. At this point, at the stage of the third cooling reactor, the sharp rise (to  $\sim 70 \text{ ppm}$ ) is attributed to the flow coming from the second reactor of the jet region, Figure 34. This reactor has an intermediate temperature between that of the flame and the one of the second effusion cooling reactor (Figure 57, upper row) and reacted or partially reacted mixture is entrained in this zone. Owing to the high temperature of the reactor and to the residence time that the mixture flowing through it has already experienced in the system, the  $NO_x$  content is higher compared to the first part of the effusion cooling liner. Therefore, the entrainment in the third near-wall reactor of part of the flow exiting this second jet-reactor causes an increase in the  $NO_x$  concentration along the liner zone. This zone is the coldest in the reactor, and the formation  $N_2O$  from NO is visible. This process is exemplified by Reaction 19, favoured below 1500 K:



The  $NO_x$  amount on the vertical profile shows higher  $NO_x$  emission for  $m_{cool} = 7.5 \text{ g/s}$ . This is attributed to the higher temperatures and the lower dilution, due to the lower amount of cooling air fed to the combustor.

#### 3.4.2.2 Effect of staging ratio

The results of the CRN fit to tracer response measured at different fuel-staging ratio are shown in Figure 60. Beside the standard operating conditions, where the fully premixed combustion is investigated, the explored staging ratios were 10%, 30% and 50%. From Figure 60 it is evident that the distribution becomes broader with increasing fuel splitting ratio, symptom of an alteration of the mixing residence times inside the combustor. The effect appears more evident on  $Out_2$ .

To describe the combustion phenomena while operating with a certain amount of fuel splitting, the network was modified, according to the explanation provided in 3.4.1.2. The image of the modified near-burner region is shown again below, in Figure 59.

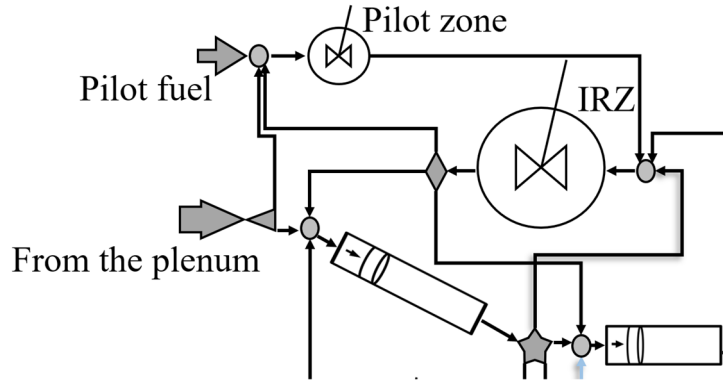


Figure 59: modified network to describe the near-nozzle region for fuel-staging operation. A CSTR reactor to exemplify the injection of the pilot-fuel has been added in the IRZ.

The mass flow entrained in the pilot reactor, as well as its volume, increases with increasing ratio of pilot fuel to main premixed fuel, Table 17. The global RTDs, Figure 61, show the early rising edge due to the entrainment from the lower path. This feature corresponds to the ensemble of peaks “1” in Figure 61. It is clearly sharper in the case of  $st. = 50\%$ , attributed to the different interaction between main flow and the effusion cooling flow at different staging ratios. The mass flow from the main zone into the cooling zone, expressed by  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ , decreases for  $st. = 10\%$  and then increases again until  $st. = 50\%$ , which exhibits an even higher value of the parameter. The staging flow creates an additional mixing volume in the combustion chamber, altering mixing times and mixing pattern. Initially, this different mixing attitude rearranges the flow such that the exchange with the effusion cooling air is lowered. While increasing the staging ratio, the additional mixing volume increases and influences the opening angle of the jet flow, possibly the cause of the increment of  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$  with the staging ratio.

It is additionally likely to be also responsible for the higher amount of flow recirculated through the ERZ. On the other hand, recirculation through the IRZ is discouraged with higher staging ratio because of the higher axial momentum of the flow, induced by the axial fuel injection and the locally higher temperatures with respect to fully premixed combustion, which cause thermal expansion. The effect on the global residence time  $\tau^m$  follows the observations from above: a small amount of pilot fuel increases the global mean residence time because of the alteration of mixing times in the flame zone, whereas a larger amount of pilot fuel above  $st. = 20\%$  increases the axial momentum and leads to a reduction of global residence times. According to  $\sigma_{tot}^2$ , in Table 17, the spread of the distribution increases with increasing pilot fuel amount, with the exception of  $st. = 30\%$ .

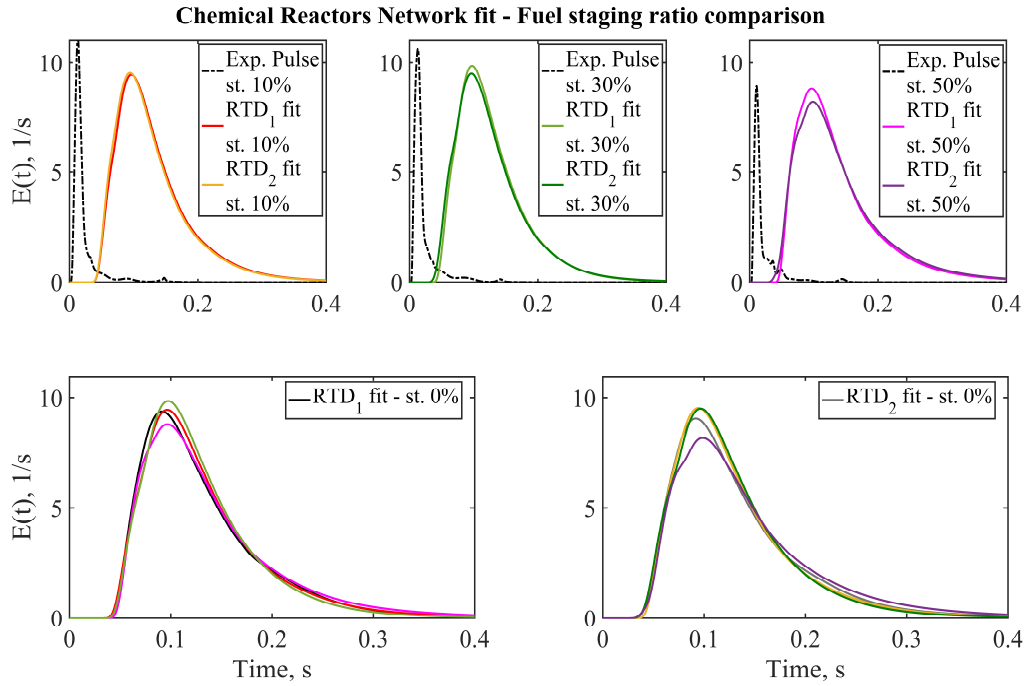


Figure 60: CRN-fit experimental tracer responses for staging ratio = 0%, 10%, 30% and 50%. Upper row:  $Out_1$  and  $Out_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

The general evolution of the distributions, Figure 61, is analogous to what explained before: there is a first increase in the  $E(t)$  due to direct entrainment in the effusion cooling region, ensemble of peaks “1”. As explained, the highest is reached for  $st = 50\%$ . The peaks “2” concern the flow evolving first in the two jet regions, and then mixing in the central exit zone, associated with higher flow velocities, see “path 1” in Figure 56. The flow that is entrained in the side reactor in the exit zone, peaks “3” in Figure 61 and “path 2” in Figure 56, reaches later the outlet of the SSGT.

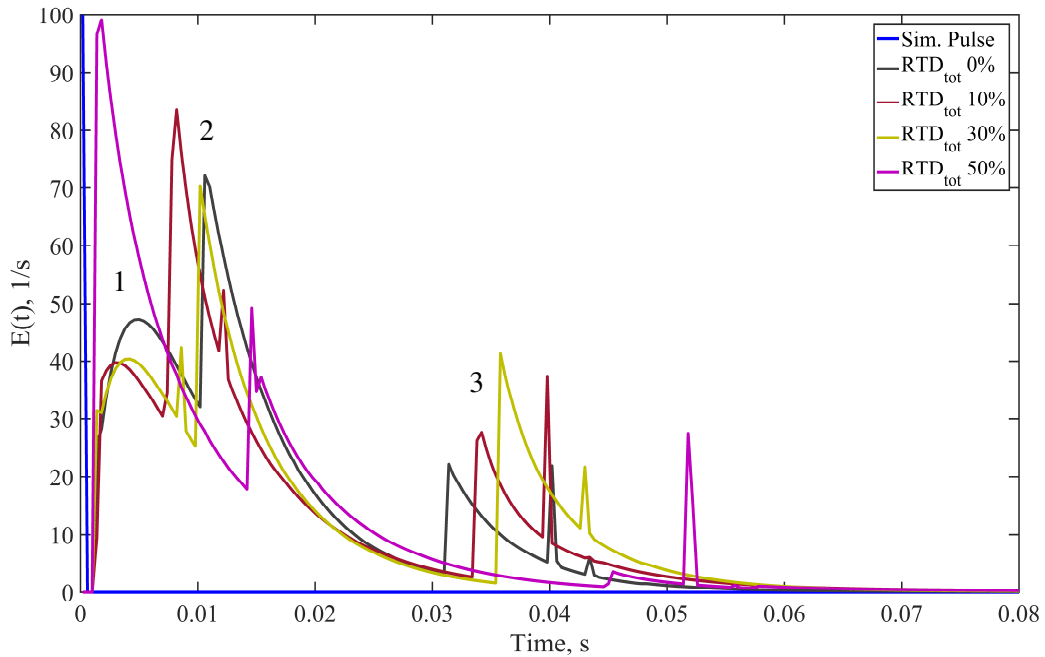


Figure 61: global RTD of the combustion chamber, staging ratio = 0%, 10%, 30% and 50%.

Figure 63 shows the influence of the pilot-splitting ratio on species formation. Before commenting on the results, an issue already mentioned in paragraph 3.3.2.3 should be addressed. In paragraph 3.3.2.3, it was stated that the kinetic model chosen to carry out the kinetic analysis was the  $C1 - C4$  mechanism, but that the *RNA* software (introduced in 2.2.2) could not always reach convergence in a reasonable time. That was the case for the boundary condition  $st. = 50\%$ . Therefore, in this case, the profiles reported in Figure 63 for this case have been calculated using the *GRI 3* mechanism. In addition to the sensitivity analysis to the employed kinetic mechanism carried out in 3.3.2.3, the suitability *GRI 3* is tested here once again, providing a comparison between the results obtained with the  $C1 - C4$  mechanism and the *GRI 3* in the case of  $st. = 30\%$ . This comparison is shown in Figure 62.

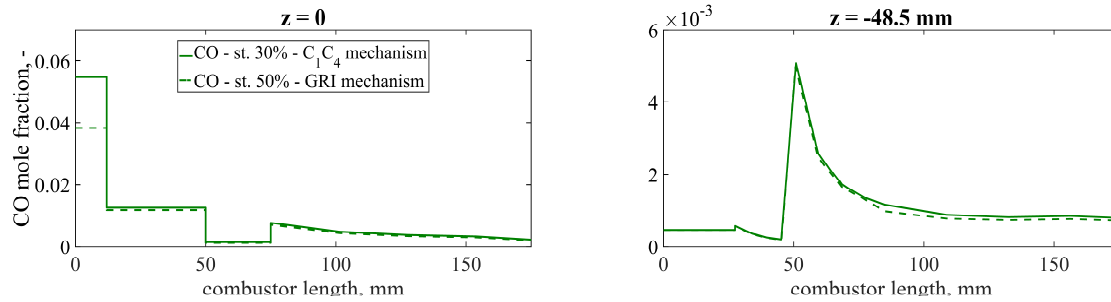


Figure 62: comparison between the  $C1 - C4$  mechanism and the *GRI 3* mechanism. This additional comparison has the aim of determining whether it is correct or not to use the *GRI 3* mechanism to evaluate the kinetics in those cases where the  $C1 - C4$  mechanism was not applicable.

The agreement between the profiles calculated with the two different kinetic mechanisms is good along the selected profiles yielding an error below 10%. An exception is evident in the first part of the centreline plot, when comparing the calculation carried out in the pilot reactor. Here the error is 40%, and the *GRI 3* heavily underpredicts CO formation in this case. However, as stated earlier, this discrepancy disappears with further mixing and reaction inside the system. Therefore, keeping in mind the chance of this discrepancy happening in the first pilot reactor, where fuel-rich conditions are established, the *GRI 3* is employed in the following discussion for the kinetic evaluation of the CRN for  $st. = 50\%$ .

Going to Figure 63, the amount of CO clearly increases while increasing the staging ratio. While, for  $st. = 10\%$  and  $st. = 30\%$ , the concentrations remain at values whose order of magnitude is comparable with those found for premixed combustion, those predicted for  $st. = 50\%$  remain higher along the whole coordinate, though showing the same trend as for the other cases. In the cooling region,  $z = -48.5$  mm in Figure 63, a high staging ratio of  $st. = 50\%$  is also responsible for the largest CO production. An only marginally increased staging ratio ( $st. = 10\%$ ) compared to the standard operating condition follows the trend seen for premixed combustion.  $st. = 30\%$  shows a lower amount of CO in the first liner reactor - analogous to  $st. = 50\%$  - but then the species mole fraction increases up to ~7000 ppm in the second liner reactor. The CO quantity gets lowered moving along the last part of the liner zone, being consumed with the advancement of mixing and chemical reaction.  $st. = 50\%$  presents the same trend as  $st. = 30\%$  in the initial part of the near wall region. Once the final cooling-zone is reached, its behaviour is completely different from the other cases: CO concentration increases to 0.02 on a mole fraction basis, and then decreases only to 0.01 along the combustion length. This is attributed to two factors: the first is the ratio of  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ , discussed earlier, the second is a different mixing behavior whose importance grows with increasing splitting ratio. Besides a higher share of the main flow mixing in the cooling path (higher  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ ) in the case  $st. = 50\%$ , a clear trend emerges from CO data regarding the axial position at which the significant exchange of mass flow between main and liner path occurs. With increasing amount of fuel fed to the pilot, the flow from the main flow zone to the initial part of the near wall reactors gets lower, resulting in less CO in an early stage with increasing staging ratio. In the second cooling reactor,  $st. = 30\%$  and  $st. = 50\%$  show approximately the same increase in CO mole fraction, because there is a more intense mixing between the parallel

paths. At the final stage, CO formation for  $st. = 50\%$  increases dramatically because in this case there is the highest entrainment of reacting flow into the cooling region. In other words, the splitting ratio shifts the axial coordinate at which the higher share of reacting flow mixes with fresh cooling air. Beside the amount of entrained flow, it is necessary to consider its CO content as well, which for  $st. = 50\%$  is high at the centreline  $z = 0$ . These factors define the different behaviour: there is a higher share of reacting mixture, containing a great amount of CO, entrained into the coldest zone of the near wall region and most likely of the reactor itself. While the cooling does not seem to pose a severe inhibition to CO oxidation in the other cases, the reaction does not significantly lower the species concentration for such high quantities of CO. On the other hand,  $st. = 30\%$  shows the same behaviour as the other two compared operating conditions in the third part of the near-wall region: to comment in a similar way as before, a lower share of reacting flow mixes in this zone, whose CO content is easily oxidized. This tendency is as well clear on the exit plane.

 Table 17: global properties of the RTDs and CRN-fit parameters,  $st. = 0\%, 10\%, 30\%$  and  $50\%$ 

	$st.$ $= 0\%$	$st. = 10\%$	$st.$ $= 30\%$	$st.$ $= 50\%$		$st.$ $= 0\%$	$st.$ $= 10\%$	$st.$ $= 30\%$	$st.$ $= 50\%$
$\tau_{tot}^m$	0.018	0.021	0.022	0.018	$\tau_{tot}^c$	0.001	0.001	0.001	0.001
$\sigma_{tot}^2$	0.0013	0.0042	0.0037	0.0057	$\tau_{tot}^{0.95}$	0.041	0.052	0.049	0.053
$S_{tot}^3$	10	7	8	7	$\tau_{tot}^{0.99}$	0.13	0.16	0.12	0.17
$m_{pilot\ reactor}$	-	0.01	0.0224	0.139	$m_{IRZ}$	6.5	3.3	4.4	1.7
$m_{total\_feed}$					$m_{in\_main}$				
$V_{pilot}$	-	$2.4 \times 10^{-4}$	0.0051	0.0086	$m_{ERZ}$	0.15	0.28	0.23	0.19
$V_{flame}$					$m_{in\_main}$				
$m_{flame}$	0.98	1.30	1.32	1.38	$m_{cooling \rightarrow main}$	0.18	0.06	0.21	0.09
$m_{in\_main}$					$m_{total\_feed}$				
$m_{main \rightarrow cooling}$	0.43	0.35	0.40	0.58	$\tau_{IRZ}$	5.8	1.13	8.7	2.40
$m_{total\_feed}$						$\times 10^{-4}$	$\times 10^{-3}$	$\times 10^{-4}$	$\times 10^{-3}$
$\tau_{ERZ}$	0.03	0.01	0.02	0.02	$\tau_{flame}$	0.0031	0.0023	0.0027	0.0022

The levels of  $C_2H_2$  formation on the centreline of the combustor show the same behaviour seen before for a variation in the cooling mass flow (see Figure 57), except for the pilot reactor. Here, rich combustion conditions are established, leading to high acetylene mole fraction. This high amount of the species is consumed in the downstream section of the combustor, though still showing higher levels for  $st. = 50\%$  at the exit plane. The  $C_2H_2$  evolution at  $z = -48.5$  shows the same trend as the carbon monoxide. A higher concentration is detected for the case  $st. = 30\%$  in the second effusion cooling region (Figure 34 as a reference).

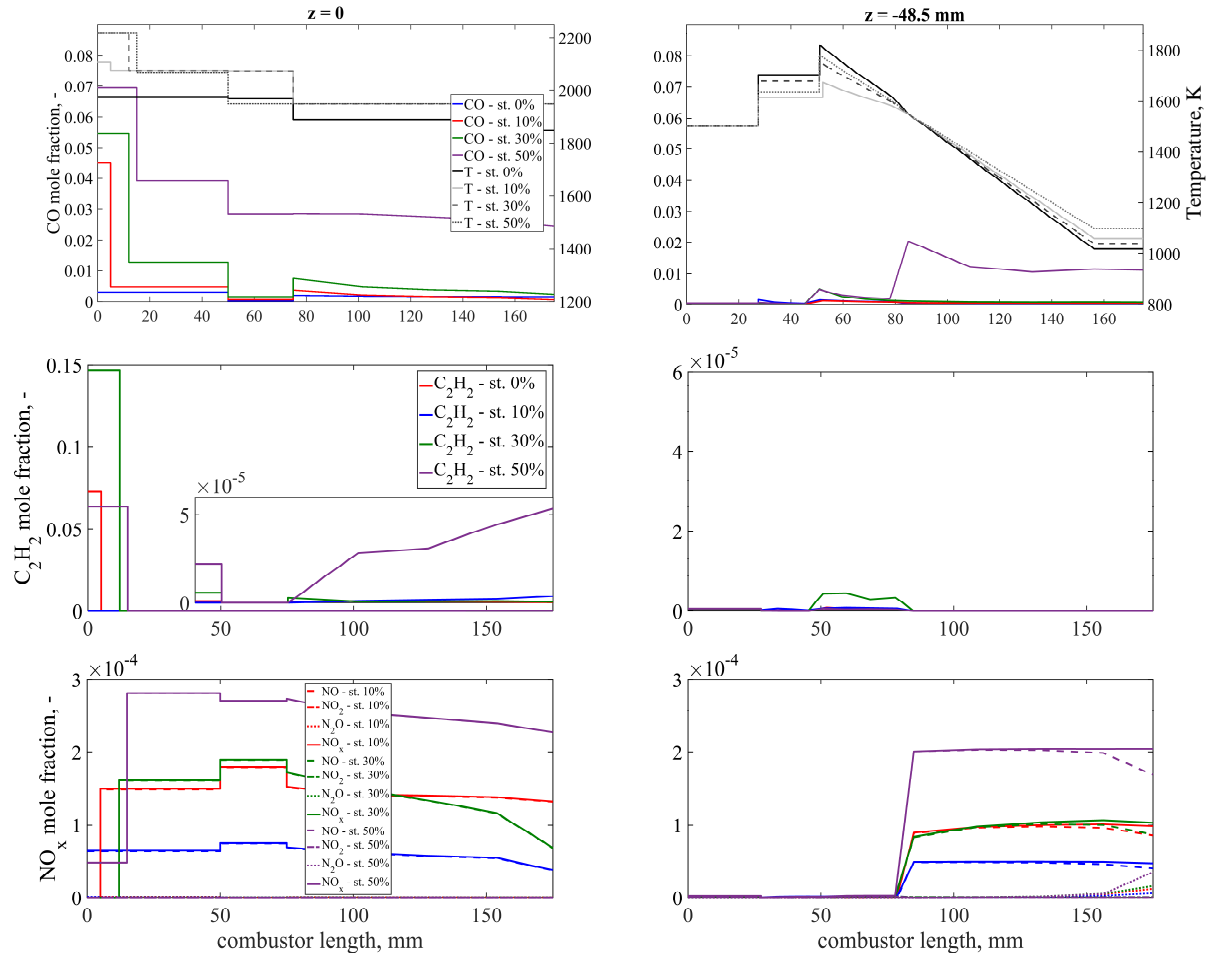


Figure 63: influence of staging ratio on species formation. Upper row: CO along selected profiles, middle row:  $C_2H_2$ , lower row:  $NO_x$ .

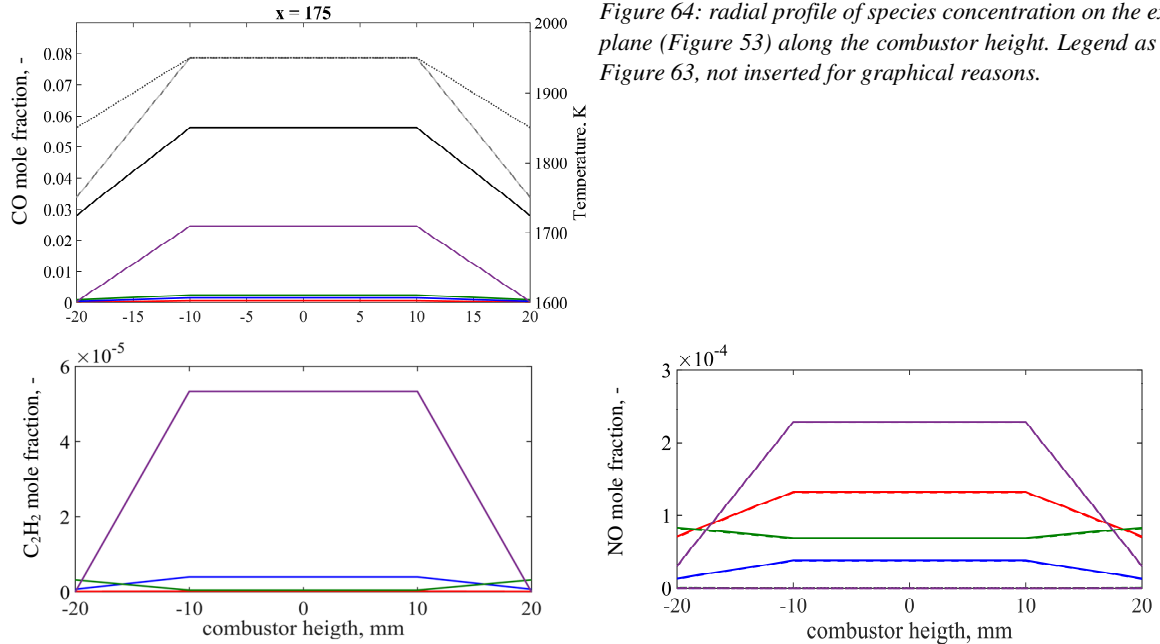


Figure 64: radial profile of species concentration on the exit plane (Figure 53) along the combustor height. Legend as in Figure 63, not inserted for graphical reasons.

$NO_x$  concentration as a function of staging ratio is given in the last row of Figure 63. The calculated species concentration equals zero in the core reactor for  $st. = 10\%$  and  $st. = 30\%$ , most likely due to the low residence times in this zone for the mentioned staging ratios. In the flame zone, the nitrogen oxides concentration rises sharply, reaching a larger value for the higher the staging ratios.  $st. = 50\%$

exhibits nonetheless a notably increased amount of these species compared to the other two cases. The  $\text{NO}_x$  concentration in the IRZ shows the slight increase seen also in Figure 57, except for the case with the highest splitting ratio: here the IRZ concentration of  $\text{NO}_x$  experiences a slight decrease instead, because of the higher  $\tau_{\text{IRZ}}$ . In the segregated exit zone, the concentration slowly decreases. The concentration of  $\text{NO}_x$  is neglectable in the effusion cooling region until the most downstream part. This part exchanges flow with the bypass around the IRZ, whose temperature is high enough to trigger  $\text{NO}_x$  production. The flow with a low nitrogen oxides content mixes in the first part of the liner zone. On the exit plane, shown in Figure 64, the  $\text{NO}_x$  concentration increases with increasing staging ratio, with the exception of the side reactor for  $st. = 50\%$ , whose concentration is comparable to the premixed case. This is attributed to the higher residence time in this zone for this condition: the passing time in this zone was found larger with increasing fuel splitting ratio. The 30% fuel splitting ratio results as the optimal operating condition for yielding the lowest  $\text{NO}_x$  concentration.

### 3.4.2.3 Effect of operating pressure

The CRN-fit for the measurements carried out at a higher pressure,  $P = 3$  bar, is shown in Figure 65. The length of the flame zone,  $l_{\text{flame}}$ , was an additional parameter of the optimization. The earlier rise of the distribution for the lower measurement location is present also for the higher-pressure case. Both high-pressure distributions appear broader than the low-pressure ones, owing to the lower flowrate in the system, though partially balanced by the higher CRN-fit temperatures. The significantly different shape of the two measurements positions for  $P = 3$  bar, evident also in peak “3” in Figure 66, is attributed to the lower mass flow exchanged from the effusion cooling path to the main path, quantified in Table 18.

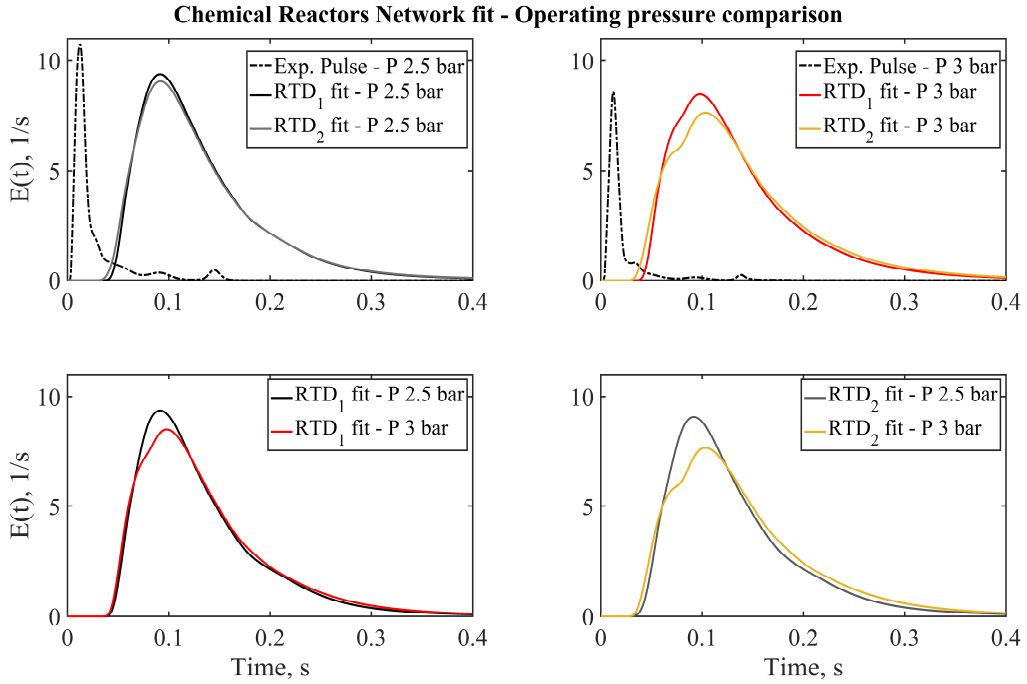


Figure 65: CRN-fit experimental tracer responses for  $P = 2.5$  bar and  $P = 3$  bar. Upper row:  $\text{Out}_1$  and  $\text{Out}_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

The global RTD for  $P = 3$  bar is shown in Figure 66, while Table 18 proposes the values of selected parameters to carry out the comparison. The distribution rises sharply after approximately 2 ms, due to the tracer entrained from the cooling flow. This event takes place earlier for  $P = 2.5$  bar than for the increased pressure, attributed to the pressure effect on the flow field. Consequently, the mean residence times  $\tau^m$  and the spreads  $\sigma^2$ , as well as  $\tau_{\text{tot}}^{0.95}$  and  $\tau_{\text{tot}}^{0.99}$  (Table 18) show increased values for a higher operating pressure. The sharper rise, and, accordingly, the sharper falling edge that characterizes the

RTD for  $P = 3$  bar is attributed to the lower  $\tau_{flame}$ , due to the concurrent effect of a lower  $l_{flame}$  and a higher mass flow into the flame region, characterized by  $\frac{m_{flame}}{m_{in\_main}}$ . Referring to the model schematization, Figure 34, the fastest path to the exit foresees entrainment in the flame zone and then in the cooling path. A lower  $\tau_{flame}$  translates to a sharper falling edge because of the lower mixing time experienced by the fluid.

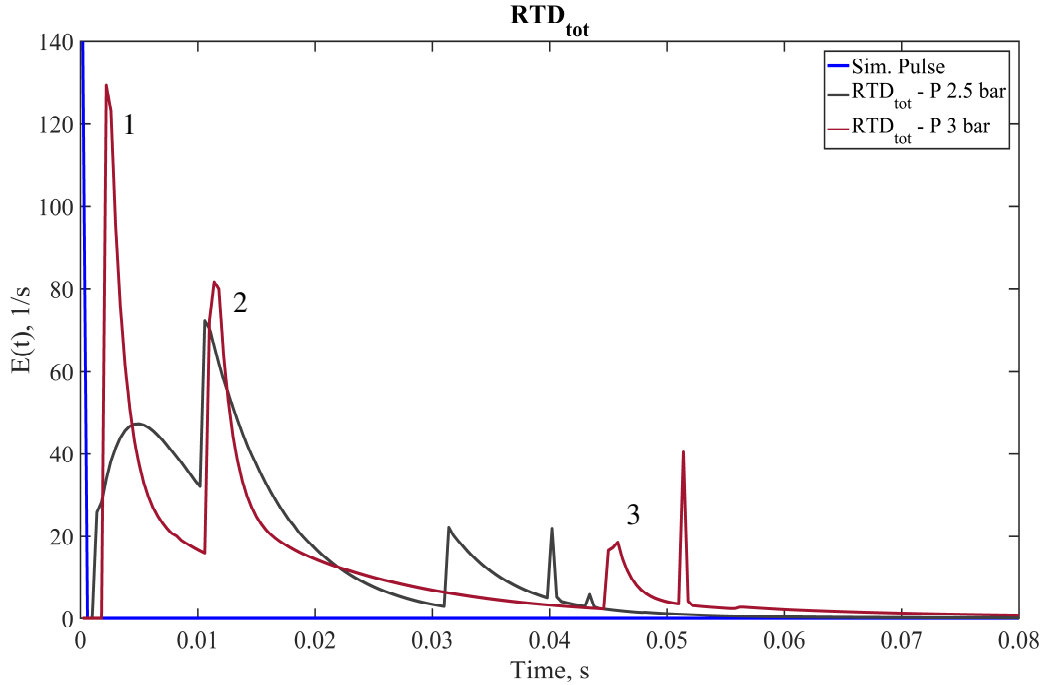


Figure 66: global RTD of the combustion chamber,  $P = 2.5$  bar and  $P = 3$  bar.

The local maximum in the RTD after  $t = 0.01$  s corresponds to the tracer carried by the part of the flow following the two jet-PFRs, and then being entrained in the central PFR in the exit region, “path 1” in Figure 56. It exhibits a sharp rise followed by a similarly sharp decay until after  $t = 0.02$  s: here the slope of the falling edge of the distribution calculated for  $P = 3$  bar lowers, possibly due to the  $\tau_{IRZ}$ , which is one order of magnitude higher for the higher pressure. Instead, the  $\tau_{ERZ}$  is slightly lower because of the higher recirculated mass flow in this region, as indicated by  $\frac{m_{ERZ}}{m_{in\_main}}$ . The peak “3” corresponds to the passage of the fluid in the jet-region and then in the side exit-PFR, and is followed by the sharp peak that characterizes entrainment of the flow in the effusion cooling region and, at a later stage, in the side exit-PFR. The interaction with the effusion cooling air path does not significantly change when considering the mass flow from the main to the cooling zone  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ , but a significant decrease by approximately a factor of three is calculated for the reverse flow  $\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$ . The lower mixing of mass from the liner path to the bulk flow is likely responsible for the delay of the peak “3”: besides the pressure effect on the flowrate, a lower amount of mass flow in the zone determines a higher passing time.



Table 18: global properties of the RTDs and CRN-fit parameters,  $P = 2.5$  bar and  $P = 3$  bar

	$P = 2.5$ bar	$P = 3$ bar		$P = 2.5$ bar	$P = 3$ bar
$\tau_{tot}^m$	0.018	0.023	$\tau_{tot}^c$	0.001	0.002
$\sigma_{tot}^2$	0.0013	0.0011	$\tau_{tot}^{0.95}$	0.041	0.067
$S_{tot}^3$	10	5	$\tau_{tot}^{0.99}$	0.13	0.17
$\underline{m_{flame}}$	0.97	1.46	$\underline{m_{IRZ}}$	6.5	1.2
$m_{in\_main}$			$\underline{m_{in\_main}}$		
$\underline{m_{main \rightarrow cooling}}$	0.43	0.46	$\underline{m_{ERZ}}$	0.15	0.31
$m_{total\_feed}$			$m_{in\_main}$		
$\underline{m_{cooling \rightarrow main}}$	0.18	0.06	$\tau_{IRZ}$	$5.8 \times 10^{-4}$	0.0051
$m_{total\_feed}$			$\tau_{ERZ}$	0.03	0.02
$\underline{m_{flame}}$	0.97	1.46	$\tau_{flame}$	0.0031	0.0014
$m_{in\_main}$					
$l_{flame}$	50	40			

The impact of the operating pressure is now discussed in terms of pollutants formation, Figure 67. Carbon monoxide along the symmetry axis of the combustor does not show significant changes, and neither does the acetylene concentration. As seen in the previous chapters, the latter species is usually zero in the regions of CO formation schematized with a CSTR. The reason lies in  $C_2H_2$  being an intermediate, directly linked to CO by Reaction 18, and indicating the progress of the reaction towards oxidized species. In a CSTR, the evolution of the reactions is not shown, and the temperatures and residence times in these CSTRs zones are such that there is no acetylene left in their product streams. The axial coordinate showing the major variation is  $z = -48.5$  mm: after similar amount of CO in the ERZ, the CO concentration drops significantly while operating with a higher pressure. Proceeding along the axial coordinate, the opposite trend is observed, with a high peak of the CO concentration for  $P = 3$  bar. The species is consumed to levels below  $\sim 500$  ppm while approaching the exit plane.  $C_2H_2$  clearly shows the same tendency. For both species, the observed profiles are caused by the different mixing behaviour attributable to the different boundary condition applied: the higher  $\frac{m_{flame}}{m_{in\_main}}$ , Table 18, causes a lower mass flow to mix with effusion cooling in an early stage. This situation changes in a later stage, where reacting mixture reaches the liner zone and mixes with fresh air. There is no significant difference in the species concentration at the exit plane,  $x = 175$  mm, see Figure 68.

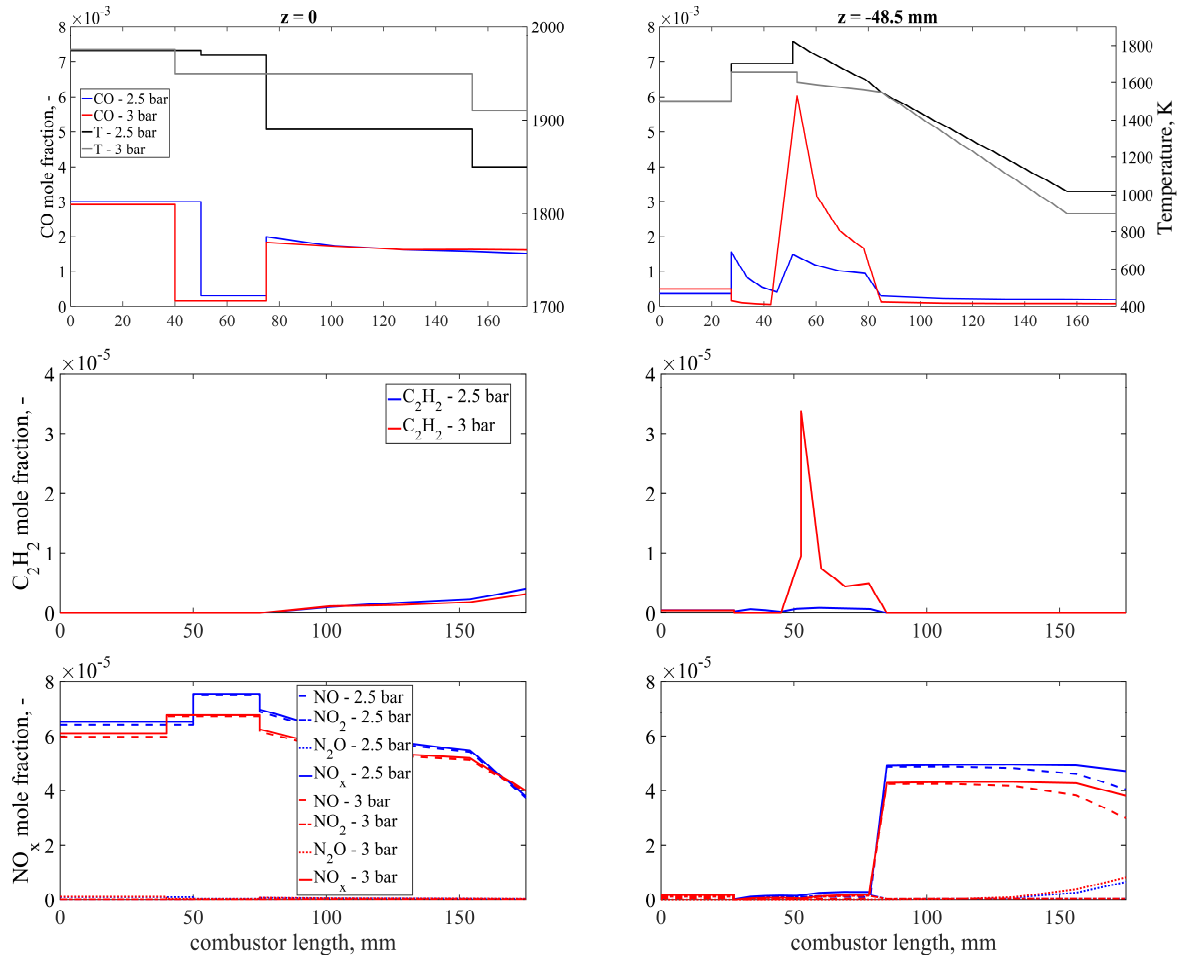


Figure 67: influence of  $P$  on species formation. Upper row:  $\text{CO}$  along selected profiles, middle row:  $\text{C}_2\text{H}_2$ , lower row:  $\text{NO}_x$ .

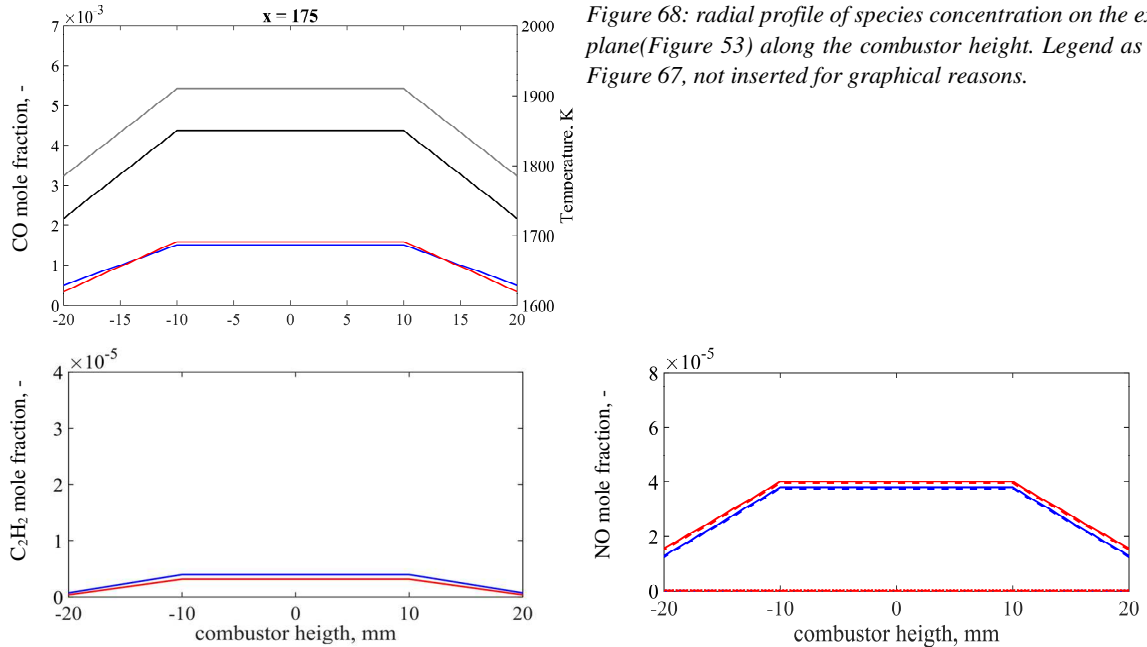


Figure 68: radial profile of species concentration on the exit plane (Figure 53) along the combustor height. Legend as in Figure 67, not inserted for graphical reasons.

Nitrogen oxides concentrations are shown in the last row of Figure 67. Starting from the combustor centreline plot, a lower in-flame  $\text{NO}$  formation is found for  $P = 3$  bar, presumably caused by a lower residence time at high temperature. Its concentration remains lower than the one at a lower pressure along the whole combustor length, though reaching the same value at the exit, as shown also for

$x = 175$  mm. The lower NO concentration in the IRZ is believed to come from the interaction between NO and CO to form  $\text{CO}_2$  and molecular nitrogen: indeed, to the lower concentration of NO in the IRZ corresponds also a lower CO concentration. Along the cooling liner, no significant amount of  $\text{NO}_x$  is calculated until the last part of the liner zone. The higher concentration in this part is attributed to mixing of flow from the main path that has experienced a sufficiently long time at high temperatures, as explained in 3.4.2.1. The  $\text{NO}_x$  amount is, in this case, lower because of the lower flow from the cooling to the main region,  $\frac{m_{\text{cooling} \rightarrow \text{main}}}{m_{\text{total\_feed}}}$  that dilutes the species concentration. As seen in the  $z = 0$  mm plot, the NO exit concentration is almost overlapping for the two cases considered.

#### 3.4.2.4 Effect of swirl number

Figure 69 compares the CRN-fit distributions for a different swirl number,  $S$ . To consider the effect of a different swirl number on the flow field, two additional parameters were added to the optimization: the reattachment length,  $l_1$  and the length of the post-flame IRZ,  $l_2$ . An estimation of these parameters was obtained in the design phase of the network based on flow field visualization data, as described in 3.3.2 and Figure 35. In accordance to [131], a lower reattachment length is found and a longer IRZ are found. The higher swirling ratio  $S$  influences the spread of the curves, as evident from Figure 69, and the effect is clearer on  $\text{Out}_2$ . The earlier rise of the  $\text{Out}_2$  curve is present in this set of measurements as well, confirming the impact of the effusion cooling air on the overall mixing characteristics.

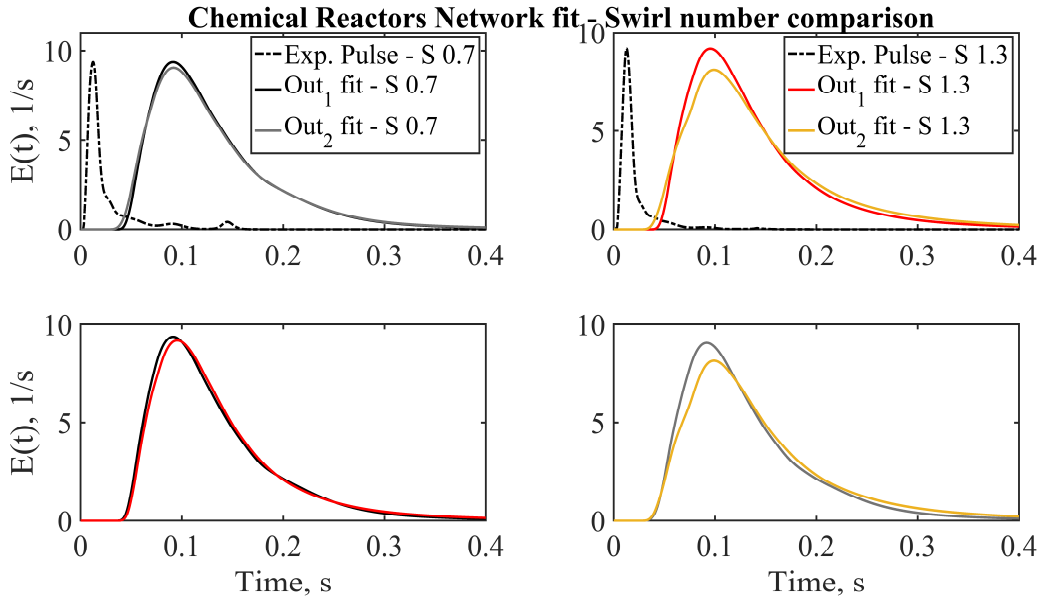


Figure 69: CRN-fit experimental tracer responses for  $S = 0.7$  and  $S = 1.3$  bar. Upper row:  $\text{Out}_1$  and  $\text{Out}_2$  for the two investigated operating conditions; lower row: comparison between the same measurement location for different operating conditions.

The effect of the different boundary condition on the RTD is given in Figure 70, and quantified in Table 19. As evident, all the parameters related to the duration of the distribution as well as the  $\sigma_{\text{tot}}^2$  yield higher values. The general behaviour, as already seen in other cases, shows a first peak pushing a part of the tracer towards the exit of the combustor after entrainment in the effusion cooling air. The sharpest shape observed for  $S = 1.3$  is attributed to the lower residence time within the flame, due to a higher mass flow involved in this zone. Referring to the model schematization, Figure 34, the fastest path to the exit foresees entrainment in the flame zone and then in the cooling path. A lower  $\tau_{\text{flame}}$  leads to sharper falling edges because of the lower mixing time experienced by the fluid. The reduced  $\tau_{\text{flame}}$  calculated for  $S = 1.3$  lies in the higher flowrate passing through this zone: a greater  $\frac{m_{\text{flame}}}{m_{\text{in\_main}}}$  is identified by virtue of the more intense mixing. Afterwards, the features stemming from both mixing in the main and liner flow path reach the exit, as described in earlier paragraphs. For a higher swirl number,

there is a larger share of mass flow entrained in the flame zone, by virtue of the more intense mixing. A higher percentage of the flow in the main path mixes with cooling air, but less cooling air is entrained to mix with the main reactive mixture. This is attributed to a larger part of the flow being pushed toward the boundaries with increasing  $S$ . The residence times in the recirculation zones is higher while operating with a higher swirl number, determining a longer distribution, as observed earlier.

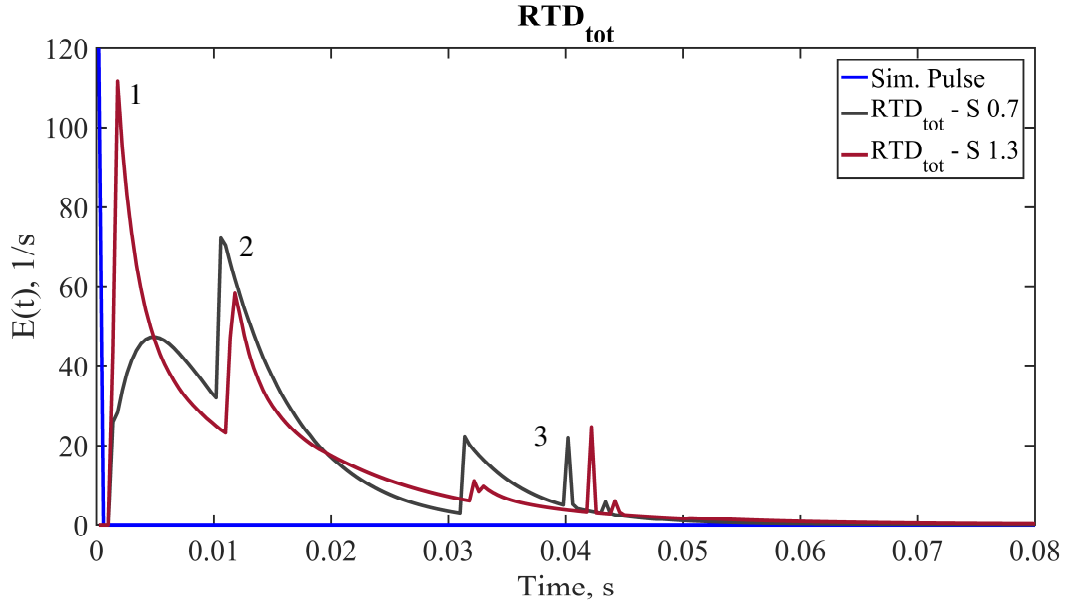


Figure 70: global RTD of the combustion chamber,  $S = 0.7$  and  $S = 1.3$ .

Table 19: global properties of the RTDs and CRN-fit parameters – swirl number  $S$  variation

	$S = 0.7$	$S = 1.3$		$S = 0.7$	$S = 1.3$
$\tau_{tot}^m$	0.018	0.019	$\tau_{tot}^c$	0.001	0.001
$\sigma_{tot}^2$	$9.069 \times 10^{-4}$	0.00104	$\tau_{tot}^{0.95}$	0.041	0.049
$S_{tot}^3$	10.26	8.201	$\tau_{tot}^{0.99}$	0.13	0.16
$\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$	0.430	0.5289	$m_{IRZ}$	6.5	1.6
$\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$	0.278	0.1951	$\frac{m_{in\_main}}{m_{ERZ}}$	0.148	0.1045
$\frac{m_{flame}}{m_{in\_main}}$	0.976	1.78	$\tau_{ERZ}$	0.0296	0.041
$\tau_{IRZ}$	0.000582	0.0032	$\tau_{flame}$	0.0031	0.0020
$l_1, mm$	35	32	$l_2, mm$	75	85

Figure 71 shows the impact of the swirl number on species formation.

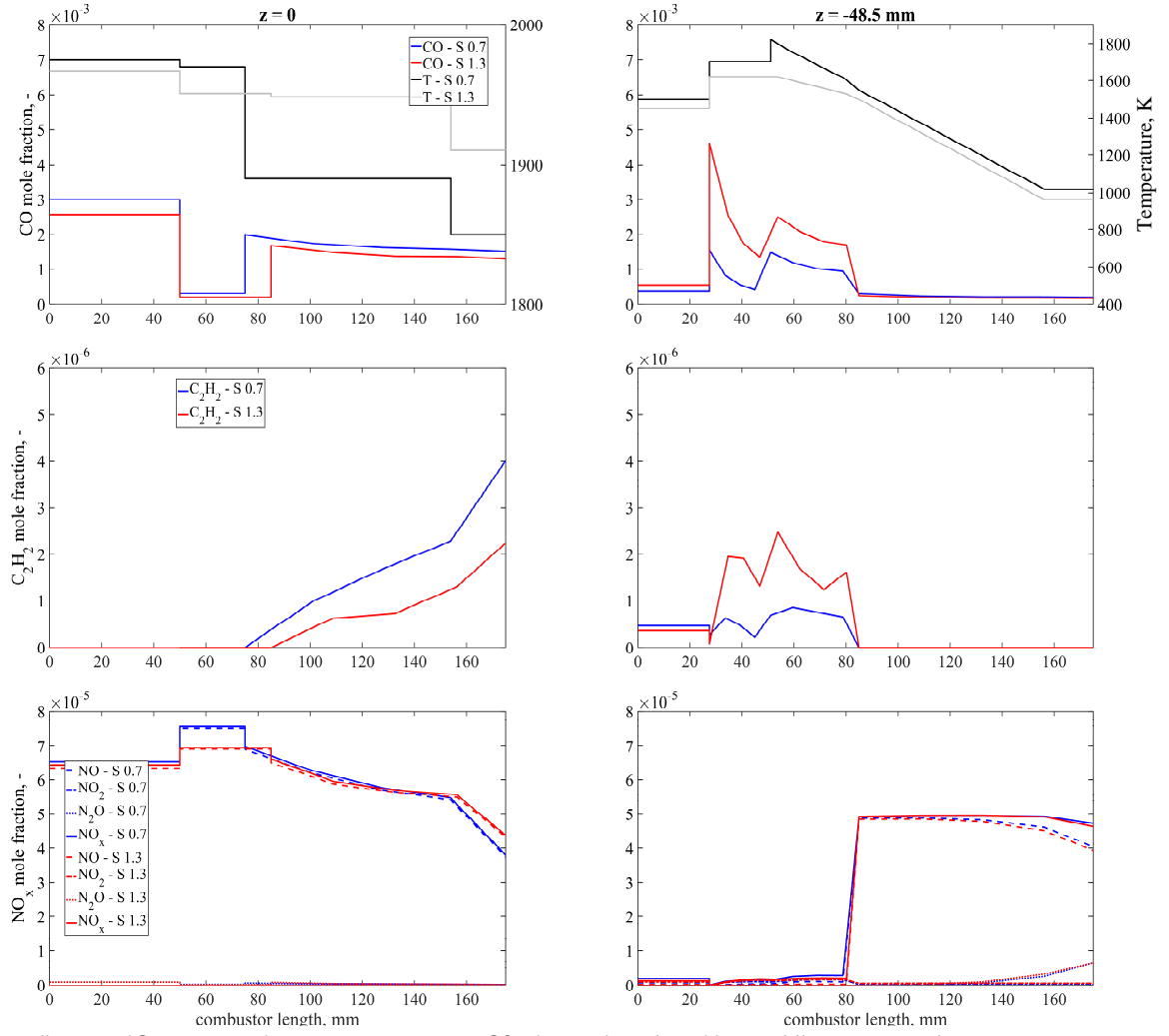


Figure 71: influence of  $S$  on species formation. Upper row: CO along selected profiles, middle row:  $C_2H_2$ , lower row:  $NO_x$ .

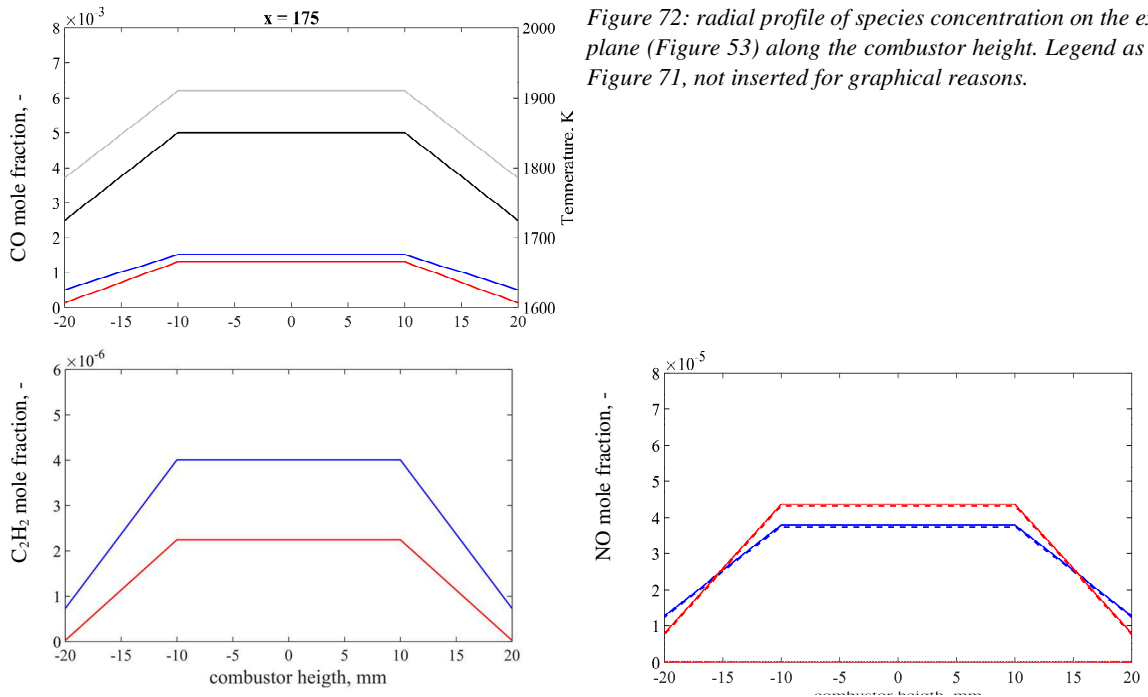


Figure 72: radial profile of species concentration on the exit plane (Figure 53) along the combustor height. Legend as in Figure 71, not inserted for graphical reasons.

Starting from the CO formation at the central axis of the combustor, it is clear that a higher  $S$  yields a lower amount of carbon monoxide along the whole combustor length, though the difference is not pronounced. The result is attributed to the more intense mixing in the near-burner region that encourages entrainment of a higher share of mass flow in the high temperature reaction zone, as quantified by  $\frac{m_{flame}}{m_{in\_main}}$ , Table 19. Instead, the parameter quantifying the amount of mass flow entrained in the post-flame IRZ is lower for  $S = 1.3$ , but it determines a higher  $\tau_{IRZ}$  (approximately one order of magnitude) with respect to the lower swirl number: therefore, less CO is calculated in this region. The CO evolution in the segregated exit region is the same for both investigated cases, and its value is slightly lower for the high-swirl case, because of the higher CO consumption highlighted before. The scenario changes when looking at the profiles in the near-effusion cooling region. Here, a higher amount of CO is formed in the first part of the liner for  $S = 1.3$ , approximately doubled with respect to  $S = 0.7$ . The reason is the higher share of reactive mixture that mixes in the near wall region, as highlighted before and as clear from the ratio  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ : the more intense mixing causes high carbon monoxide levels in the first part of the liner wall. However, the carbon monoxide content in the last part of the effusion cooling is low and approximately the same as the one observed in the case of  $S = 0.7$ . The reason lies in the high average temperature of the middle part of the plot, encouraging CO reduction, and in the mixing with the bulk flow: this flow has a low CO content. As anticipated before, the CO content at the exit of the combustor is lower while adopting a higher swirl number, and the difference is more pronounced in the lateral part of the combustor.

Just a few ppm of  $C_2H_2$  is present, and its evolution follows that of CO, though the order of magnitude is significantly lower. This species is absent in the CSTR zones, where it completely reacted to form combustion products. Its formation is appreciable in the exit-zone central PFR, where bypasses from the near nozzle region bring unreacted mixture. In the near-wall reactors, a few ppm are formed as a consequence of the flow mixing from the main flow region.  $C_2H_2$  on the exit plane, in Figure 72, is significantly lower for a higher swirl number, presumably because of the lower amount of fuel bypass that reaches this zone. This parameter has not been selected to carry out the comparison among the different operating conditions, but it is, in this case, an explanation to the lower amount of  $C_2H_2$  at the exit of the combustor: the bypass fuel for  $S = 1.3$  is approximately half with respect to the same quantity for  $S = 0.7$ . This is likely to cause the difference in the concentration of  $C_2H_2$  on the exit plane. Therefore, a higher swirl enhances the conversion limiting the amount of bypass fuel.

The  $NO_x$  concentrations present a rather identical evolution along the central axis of the combustor, except in the IRZ, where a lower swirl number yields a higher amount of pollutant species. The trend changes in the central PFR of the exit region, where the  $NO_x$  amount becomes slightly larger for a higher swirl number. The scenario at  $z = -48.5 \text{ mm}$  is the same encountered up to now: the  $NO_x$  level is low (sub-ppm) until the last part of the effusion cooling liner, then it rapidly reaches  $\sim 50$  ppm. This is attributed to the longer residence time of the mixture in a high temperature environment before mixing in this region. The flue gases reaching this point have spent more time in the system with respect to that mixing earlier in the liner-zone. Therefore, its  $NO_x$  content is higher, and it mixes in a cold region, freezing the reaction, until the nitrous oxide reaction starts, consuming NO and producing  $N_2O$ . On the exit plane, a higher  $NO_x$  mole fraction is associated with a higher swirl number, while observing the central exit PFR, but is lower at the side, which is the zone that experiences the more intense mixing due to the high swirl motion.

### 3.4.2.5 Effect of equivalence ratio

The effect of stoichiometry on the tracer response of the system is reported in Figure 73. Three different equivalence ratios were investigated (Table 2 and Table 8):  $\varphi = 0.65$ ,  $\varphi = 0.75$  and  $\varphi = 0.85$ . As shown in the magnification, the rising edges of the distributions follow the trend of the average temperature in the combustion chamber: the higher the equivalence ratio (hence, higher average temperature) the earlier the tracer response starts. This phenomenon is more pronounced while

comparing  $\phi = 0.65$  and  $\phi = 0.75$ . The impact of cooling air entraining part of the tracer and transporting it towards the exit earlier than the main flow is clear for all investigated equivalence ratios. An additional parameter was considered for the optimization in this case: the length of the flame zone,  $l_{flame}$ , Table 20.

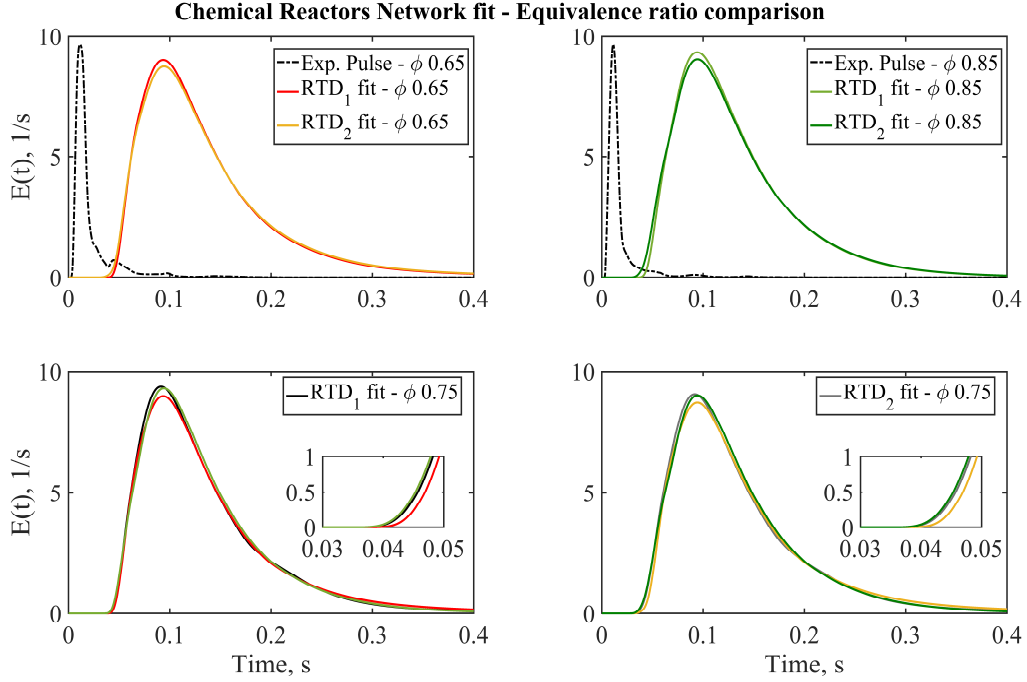
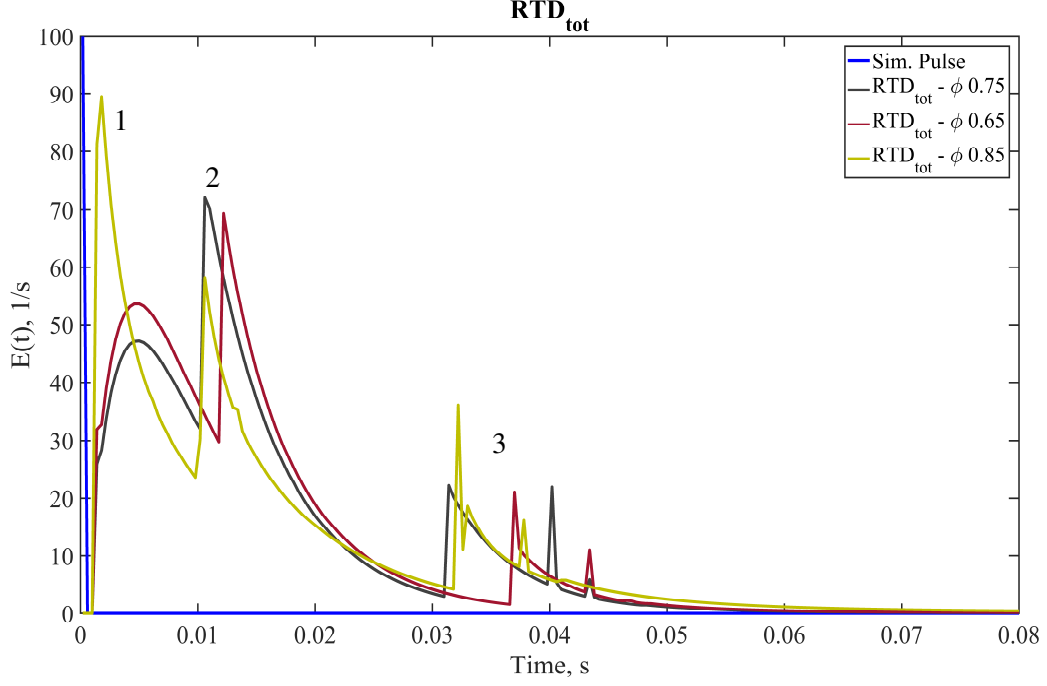


Figure 73: CRN-fit experimental tracer responses for  $\phi = 0.65$ ,  $\phi = 0.75$  and  $\phi = 0.85$ . Upper row:  $Out_1$  and  $Out_2$  for  $\phi = 0.65$  and  $\phi = 0.85$ ; lower row: comparison between the same measurement location for different  $\phi$ .

The RTD calculated using a mathematically generated pulse is presented in Figure 74. A higher initial peak is associated with entraining of the tracer in the effusion cooling path, consistent with the larger amount of  $\frac{m_{main \rightarrow cooling}}{m_{total\_feed}}$ .  $\phi = 0.85$  exhibits a sharpest shape for its peak “1”, compared to the other two cases: it is attributed to the lower residence time in the flame (Table 20), due to a higher mass flow involved in this zone. Referring to Figure 33 and Figure 34, the fastest path to the exit foresees entrainment in the flame zone and then in the cooling path. A lower  $\tau_{flame}$  translates to a lower mixing time experienced by the fluid, hence a sharper falling edge. A reduced  $\tau_{flame}$  calculated for  $\phi = 0.85$  - despite a larger flame zone - has been identified, which lies in the higher flowrate passing through this zone: a greater  $\frac{m_{flame}}{m_{in\_main}}$  and a higher temperature is experienced within this zone by virtue of the increased fuel quantity in the system. These two factors are not balanced by the increased  $l_{flame}$ , resulting anyway in a lower  $\tau_{flame}$ . After the first fast arrival of part of the tracer at the exit of the combustor, the evolution of the fluid history continues following the other possible routes inside the combustor: the ensemble of peaks “2” concerns the fluid whose evolution in the main path ends following the faster region identified on the centreline of the combustor (Figure 33 and Figure 34), whereas the remaining flow is entrained in the side zone of the segregated region of the combustor. The ratio  $\frac{m_{cooling \rightarrow main}}{m_{total\_feed}}$  increases from  $\phi = 0.65$  to  $\phi = 0.75$ , most likely because of the increased impulse towards the wall-zone imputable to the higher temperatures linked to the equivalence ratio. The mentioned parameter slightly decreases while increasing  $\phi$  further. This phenomenon is attributed once again to the increased impulse due to the higher temperatures and thus thermal expansion: it is indeed responsible for a certain share of mass flow mixing in the cooling region. However, the higher flow inertia caused by the combustion-induced acceleration pushes forward a higher share of the flow in the case of  $\phi = 0.85$  with respect to  $\phi = 0.75$ .


 Figure 74: global RTD of the combustion chamber,  $\varphi = 0.65$ ,  $\varphi = 0.75$  and  $\varphi = 0.85$ .

The flow acceleration caused by combustion is also responsible for the trend identified for the parameter  $\frac{m_{IRZ}}{m_{in\_main}}$ : the higher the flow inertia, the lower the relative centrifugal forces that cause the flow recirculation in the IRZ [123]. Therefore,  $\tau_{IRZ}$  increases with the equivalence ratio. The mass entrained in the ERZ decreases going from  $\varphi = 0.65$  to  $\varphi = 0.75$ , in accordance to the increased velocities that push the flow forward. However, this parameter increases for  $\varphi = 0.85$ . This is most likely due to the higher intensity of the ERZ with increasing equivalence ratio, due to the higher temperatures and more intense gas expansion [132]. A higher  $\tau_{tot}^m$  characterizes the richer operating condition, directly linked to the higher  $\tau_{IRZ}$ . The  $\sigma_{tot}^2$  takes its higher value in the leaner case, in accordance the longer distributions generated by lower temperatures in the system.

 Table 20: global properties of the RTDs and CRN-fit parameters – equivalence ratio  $\varphi$  variation

	$\varphi = 0.65$	$\varphi = 0.75$	$\varphi = 0.85$		$\varphi = 0.65$	$\varphi = 0.75$	$\varphi = 0.85$
$\tau_{tot}^m$	0.018	0.018	0.019	$\tau_{tot}^c$	0.001	0.001	0.001
$\sigma_{tot}^2$	0.001	$9 \times 10^{-4}$	$7 \times 10^{-4}$	$\tau_{tot}^{0.95}$	0.044	0.041	0.053
$S_{tot}^3$	9	10	5	$\tau_{tot}^{0.99}$	0.15	0.13	0.14
$m_{main \rightarrow cooling}$	0.49	0.43	0.51	$m_{IRZ}$	7.5	6.5	1.7
$m_{total\_feed}$				$m_{in\_main}$			
$m_{cooling \rightarrow main}$	0.17	0.28	0.24	$m_{ERZ}$	0.30	0.15	0.35
$m_{total\_feed}$				$m_{in\_main}$			
$m_{flame}$	0.97	0.98	1.5	$\tau_{flame}$	0.0029	0.0031	0.0021
$m_{in\_main}$				$\tau_{ERZ}$	0.02	0.03	0.01
$\tau_{IRZ}$	0.00058	0.00058	0.0025				
$l_{flame}, mm$	47	50	54				

The profiles of selected species along representative coordinates inside the combustor are shown in Figure 75 and Figure 76. The upper row is dedicated to  $CO$ . Along the combustor centreline,  $z = 0 \text{ mm}$ , the flame zone is the first one starting from the left side.



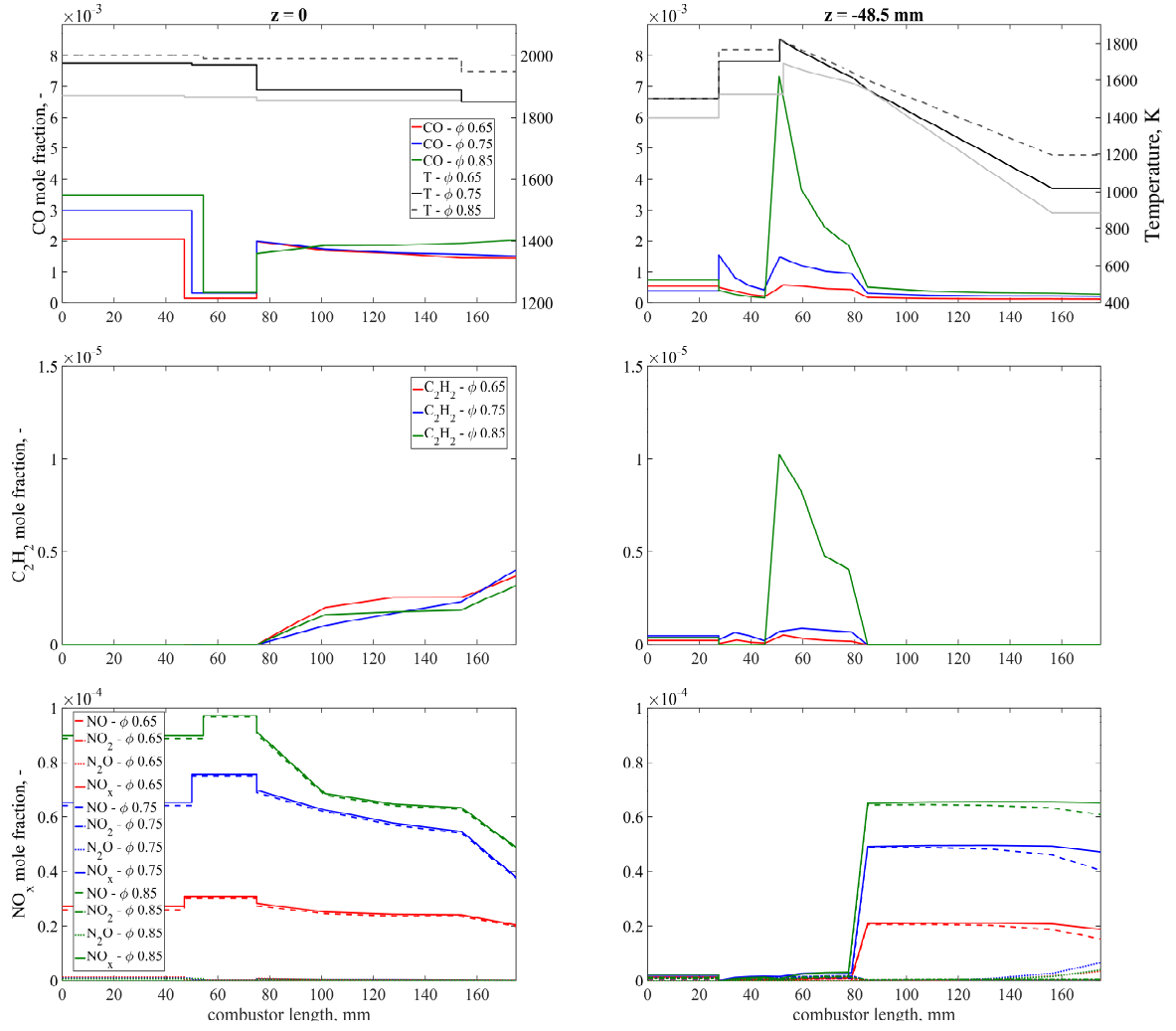


Figure 75: influence of  $\phi$  on species formation. Upper row: CO along selected profiles, middle row:  $C_2H_2$ , lower row:  $NO_x$

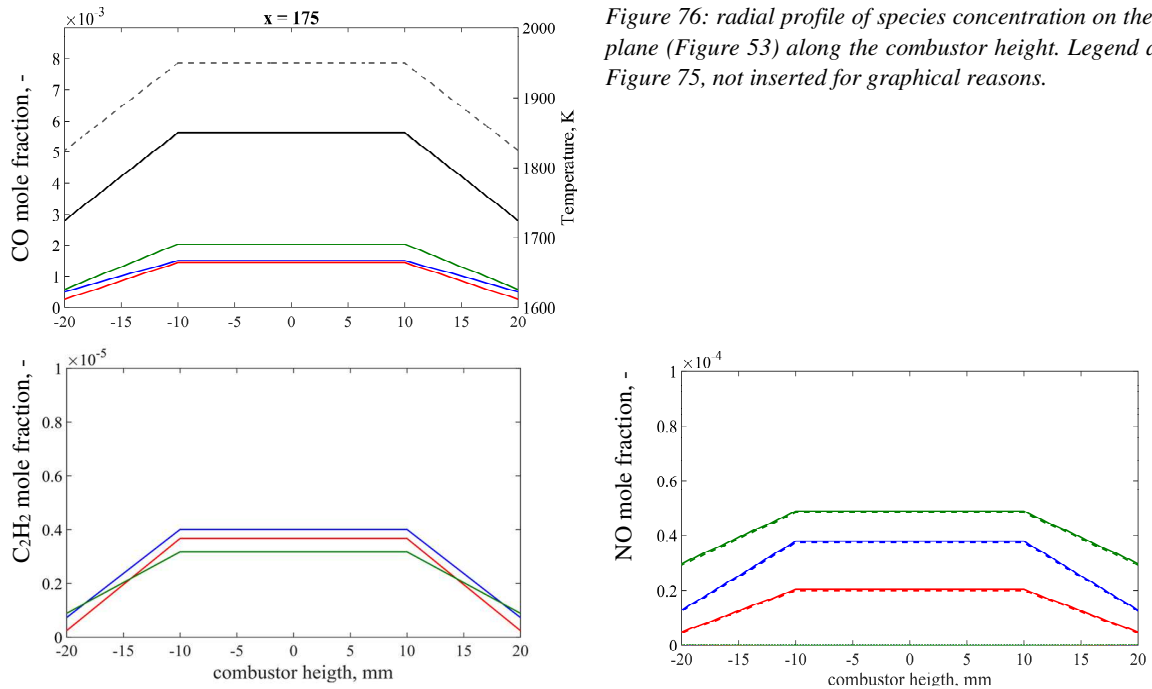


Figure 76: radial profile of species concentration on the exit plane (Figure 53) along the combustor height. Legend as in Figure 75, not inserted for graphical reasons.

Here, the  $CO$  concentration follows the equivalence ratio, increasing as the mixture becomes richer. In the IRZ,  $\varphi = 0.75$  and  $\varphi = 0.85$  show the same  $CO$  mole fraction, while  $\varphi = 0.65$  has a lower  $CO$  content.  $\varphi = 0.65$  and  $\varphi = 0.75$  exhibit the same behaviour in the exit zone PFR: more  $CO$  is formed due to flow bypasses from the near burner region, and its concentration lowers towards the exit due to mixing and reaction.  $\varphi = 0.85$  presents an increasing concentration of carbon monoxide in the beginning of the zone, that stays almost constant until the exit. The different trend of this operating condition with respect to the other two is consistent with the higher percentage of unreacted mixture reaching the exit of the system (see the reactive flow CRN, Figure 33 and Figure 34, blue dotted line). Once again due to higher flow inertia, an increased quantity of unreacted fuel is pushed towards the exit, reacting in the exit PFR.

For  $z = -48.5\text{ mm}$ , the  $CO$  concentration along the ERZ and the effusion cooling liner is given. The ERZ shows a higher carbon monoxide content with increasing  $\varphi$ , independently from the different  $\tau_{ERZ}$ . The start of the effusion cooling liner at  $x = 27.5\text{ mm}$  is characterized by a  $CO$  increase for the mid-equivalence ratio value, but both richer and leaner conditions exhibit a decrease in the species concentration, due to the different interaction with cooling air at this stage: clearly a lower amount of mixture carrying reactive species is entrained at this stage. The trend changes moving along the combustor length. In the second near wall region,  $\varphi = 0.65$  and  $\varphi = 0.75$  show the same trend, though with a lower intensity for the leaner case: reactive mixture is transported from the bulk flow region and reacts with incoming air to slowly consume the  $CO$ , dropping its concentration. The richer condition instead shows a noticeably higher  $CO$  concentration, due to the higher mixing of main flow in this region of the combustor. Nevertheless, the carbon monoxide formed in this zone is oxidized, reaching the same concentration level as the other two operating conditions at the end of the liner. The concentrations calculated on the vertical exit plane reproduce those already seen in the last part of the centreline profile. Acetylene shows the same behaviour seen in other cases. The species is not present in the flame and IRZ zones of the combustor owing to the high temperatures and suitable residence times to consume the available  $C_2H_2$ . Traces of the compound are produced in the last PFR as a result of flow bypasses carrying fuel from the inlet nozzle. The acetylene evolution along the effusion cooling liner follows the one explained for carbon monoxide.

The  $NO_x$  concentration along the selected profiles is shown in the last row. The in-flame content increases with the equivalence ratio, and, therefore, the temperature. This trend is kept in all the presented plots.

### 3.4.2.6 Summary

In this chapter, the impact of the operating conditions on the RTD and species formation in the SSGT has been described referring to the standard operation point. The relevant parameters that characterize this point are summarized again below, in Table 21.

Table 21: relevant parameters of the standard operation point.

Operation point, units		
Preheating temperature	623	K
System pressure, $P$	2.5	bar
Main air mass flow, $m_{in\_main}$	30	g/s
Equivalence ratio, $\varphi_{lean\text{ premixed}}$	0.75	[-]
Swirl number, $S$	0.7	[-]
Effusion cooling mass flow, $m_{cool}$	15	g/s
Fuel staging ratio, $st$ .	0%	[-]

To provide a last comparison among the investigated sets of boundary conditions, selected relevant parameters are listed in Table 22 and Table 23. Besides the global mean residence time inside the

combustor,  $\tau_{tot}^m \cdot \frac{m_{recirculation}}{m_{in\_main}}$  represents the total share of entrained flow in the recirculated regions with respect to the total air mass flow introduced at the entrance nozzle, and  $\frac{m_{main\_cooling}}{m_{total\_feed}}$  calculates the ratio of the total mass flow exchanged between the two flow paths (main and cooling) with respect to total air mass flow (main plus effusion cooling) fed to the system. A final overview is also given in terms of pollutants emission. The quantities  $CO_{global}$ ,  $C_2H_{2global}$  and  $NO_{global}$  in Table 22 are calculated as the weighted mean of the concentration of the species at the exit plane,  $x = 175 \text{ mm}$ . The equilibrium value for the same species is reported. This equilibrium value has been calculated in an isothermal PFR at  $T = 1800 \text{ K}$ . This temperature was chosen as a mean reactive temperature, indicating an average thermal state of the mixture in the bulk flow. Furthermore, using the same temperature for all computations enables recognizing trends depending on the specific operating condition. The deviation from the equilibrium values (calculated as  $CO_{global} - CO_{equilibrium}$ ) is also reported for the sake of a faster comparison ( $CO_{deviation}$ , and  $NO_{deviation}$ ).

Table 22: comparison among the different investigated operating points – part one

	Basic operating point (Table 21)	$m_{cool} = 7.5 \text{ g/s}$	$P = 3 \text{ bar}$	$\varphi = 0.65$	$\varphi = 0.85$
$\tau_{tot}^m$	0.018	0.020	0.023	0.018	0.019
$\tau_{flame}$	0.0031	0.0028	0.0014	0.0029	0.0021
$\frac{m_{main\_cooling}}{m_{total\_feed}}$	0.71	0.60	0.52	0.67	0.75
$\frac{m_{recirculation}}{m_{in\_main}}$	6.7	5.2	1.5	7.8	2
$CO_{global}$	$7.6 \times 10^{-4}$	$8.7 \times 10^{-4}$	$7 \times 10^{-4}$	$6.3 \times 10^{-4}$	0.001
$C_2H_{2global}$	$1.5 \times 10^{-6}$	$2.0 \times 10^{-6}$	$1.2 \times 10^{-6}$	$1.2 \times 10^{-6}$	$1.3 \times 10^{-6}$
$NO_{global}$	$3.7 \times 10^{-5}$	$7 \times 10^{-5}$	$3.1 \times 10^{-5}$	$1.6 \times 10^{-5}$	$6.8 \times 10^{-5}$
$CO_{equilibrium}$	$2.1 \times 10^{-5}$	$2.8 \times 10^{-5}$	$1.9 \times 10^{-5}$	$1.7 \times 10^{-5}$	$2.8 \times 10^{-5}$
$C_2H_{2equilibrium}$	0	0	0	0	0
$NO_{equilibrium}$	0.0028	0.0013	0.0028	0.0030	0.0025
$CO_{deviation}$	$7.4 \times 10^{-4}$	$8.4 \times 10^{-4}$	$6.8 \times 10^{-4}$	$6.1 \times 10^{-4}$	$9.7 \times 10^{-4}$
$NO_{deviation}$	$-2.8 \times 10^{-3}$	$-1.2 \times 10^{-3}$	$-2.8 \times 10^{-3}$	$-3 \times 10^{-3}$	$-2.4 \times 10^{-3}$

Table 23: comparison among the different investigated operating points – part two

	Basic operating point (Table 21)	$S = 1.3$	st. = 10%	st. = 30%	st. = 50%
$\tau_{tot}^m$	0.018	0.019	0.021	0.022	0.017
$\tau_{flame}$	0.0031	0.0020	0.0023	0.0027	0.0022
$\frac{m_{main\_cooling}}{m_{total\_feed}}$	0.71	0.72	0.40	0.61	0.68
$\frac{m_{recirculation}}{m_{in\_main}}$	6.7	1.7	3.6	4.6	1.8
$CO_{global}$	$7.6 \times 10^{-4}$	$5.6 \times 10^{-4}$	$4.7 \times 10^{-4}$	0.0015	0.011
$C_2H_{2global}$	$1.5 \times 10^{-6}$	$7.0 \times 10^{-7}$	$1.1 \times 10^{-7}$	$1.3 \times 10^{-6}$	$1.6 \times 10^{-5}$
$NO_{global}$	$3.7 \times 10^{-5}$	$4.1 \times 10^{-5}$	$1.0 \times 10^{-4}$	$9.8 \times 10^{-5}$	$9.8 \times 10^{-5}$
$CO_{deviation}$	$7.4 \times 10^{-4}$	$5.4 \times 10^{-4}$	$4.5 \times 10^{-4}$	$1.5 \times 10^{-3}$	$1 \times 10^{-2}$
$NO_{deviation}$	$-2.8 \times 10^{-3}$	$-2.7 \times 10^{-3}$	$-2.7 \times 10^{-3}$	$-2.7 \times 10^{-3}$	$-2.7 \times 10^{-3}$

The highest  $\tau_{tot}^m$  is attributed to  $P = 3$  bar, most likely due to the pressure effect on the flow rate of the system and to the large value of  $\tau_{IRZ}$  (see Table 12). This agrees with the value of the parameter  $\frac{m_{recirculation}}{m_{in\_main}}$  being the lowest in the system, accompanied by an increased value of the IRZ volume in view of a smaller flame. The global mass flow exchanged between the effusion cooling path and the main path is lower with respect to the standard operation point.  $P = 3$  bar shows a lower global concentration of pollutants reaching the exit plane. The CO value agrees with the pressure effect on the equilibrium concentration, while the result for NO is attributed to the lower  $\tau_{flame}$ .

Decreasing  $m_{cool}$  increases the  $\tau_{tot}^m$  species spend in the system, because of the lower flow rate globally fed to the combustor and because of a slightly lower  $\frac{m_{recirculation}}{m_{in\_main}}$ , that increases residence times in recirculation zones. The lower  $\frac{m_{recirculation}}{m_{in\_main}}$  stems from the higher temperatures of the system, due to a lower amount of cooling air. As expected, introducing a lower amount of air along the effusion liner lowers the interaction between the bulk flow and flow in the lower part of the combustor. The concentration of pollutants at  $x = 175$  mm is higher, partly for a global concentration effect, as indicated by the equilibrium value. The amount of  $NO_{global}$  is indeed noticeably higher. Referring to Figure 57, this increase might come from the higher in-flame concentration, attributed to the higher temperature.

A higher equivalence ratio shows a larger value of  $\tau_{tot}^m$ , likely because of the lower entrainment of flow in the IRZ, which causes a higher residence time in this perfectly mixed zone. Accordingly, the parameter  $\frac{m_{recirculation}}{m_{in\_main}}$  decreases if the  $\varphi$  is increased.  $\tau_{flame}$  shows its lower value while adopting  $\varphi = 0.85$ , because more mass flow is entrained in this zone and the flame temperature is higher. The interaction between the two flow paths inside the combustor, quantified by the parameter  $\frac{m_{main\_cooling}}{m_{total\_feed}}$ , becomes larger going from  $\varphi = 0.65$  to  $\varphi = 0.85$ . The species concentration follows the same trend. A higher swirl number increases the mixing times resulting in broader distributions. The swirl entrains more mass flow in the flame zone, resulting in a lower  $\tau_{flame}$ . The tendency of the flow to be entrained in recirculation zones is reduced, and  $\frac{m_{main\_cooling}}{m_{total\_feed}}$  is similar for the low and high swirl number. Carbon-based pollutants are drastically reduced for  $S = 1.3$ , by virtue of the high mixing and the lower amount of fuel bypass, explained in 3.4.2.4. The slightly higher value of  $NO_{global}$  is attributed to a temperature effect:  $S = 1.3$  shows a higher post-flame temperature with respect to  $S = 0.7$ .

An increasing staging ratio increases  $\tau_{tot}^m$  until  $st. = 30\%$ , then the mean residence time in the combustor experiences a decrease, attributed to the higher average temperature in the system. The in-flame residence time is globally lower with respect to premixed combustion, though exhibiting a maximum for  $st. = 30\%$ . For staged operation, the mass flow entrained in the flame increases with increasing staging ratio. Besides, there is an additional volume, the pilot reactor, that increases with increasing staging ratio. Therefore,  $\tau_{flame}$  stems from the concurrent effects of a different flame volume and an increased in-flame mass flow.  $\frac{m_{recirculation}}{m_{in\_main}}$  is lower for partially premixed combustion with respect to purely premixed, and exhibits a maximum, once again, in the case of  $st. = 30\%$ . The interaction between the main flow path and the cooling air is lower for all staging cases with respect to the absence of staging. Nevertheless, the global amount of mass flow exchanged between the two paths,  $\frac{m_{main\_cooling}}{m_{total\_feed}}$ , increases together with the staging ratio. The same trend is followed by the species concentration. However,  $st. = 10\%$  exhibits a lower amount of  $CO_{global}$ .

A final overview is additionally given in terms of exit temperature profile. The interest towards the temperature profile at the exit of the gas turbine combustor is high, because this parameter is crucial for the durability of the turbine. A uniform temperature profile would be ideal, whereas a high level of non-homogeneity is harmful for the turbine because it causes local hot spots that decrease the life of the turbine. Non-uniform temperature profiles at the exit of the combustor are referred as hot streaks [133],

[134] and efforts to improve the mixing inside the combustor in order to reduce the non-homogeneity of the temperature profile have been made [135]. Given the technological relevance of this topic, the temperature profile at  $x = 175 \text{ mm}$ , showing the behaviour along the lower half of the combustor, is given in Figure 77.a. Figure 77.b shows the difference between the maximum and the minimum temperature at the same location as, to give an idea of the inhomogeneity for each tested operation point. The temperatures presented are those fitted by the optimization procedure while fitting the CRN to the tracer response. The description “standard” refers to the boundary conditions that characterize the standard operation point.

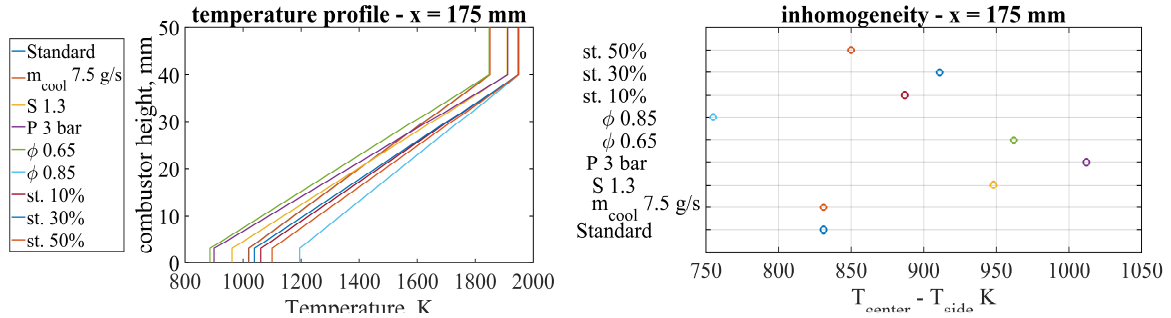


Figure 77: **a**, temperature along a vertical profile at  $x = 175 \text{ mm}$ ; **b**: difference between the maximum and minimum temperature along the vertical profile at  $x = 175 \text{ mm}$ .

From Figure 77.b, it emerges that the higher equivalence ratio that was tested exhibits the lowest value of the temperature difference. The highest value of the parameter chosen to quantify the inhomogeneity occurs while operating the system with a higher pressure. The standard operation point and the lower  $m_{cool}$  operation point show the same value, almost 100 K higher with respect to the same difference at  $\phi = 0.85$ . From Figure 77 emerges that a higher equivalence ratio results in a lower value of the inhomogeneity parameter, most likely attributable to the higher amount of fuel introduced in the system that is then entrained and mixed in the different reaction zones. A clear trend is not identified for the fuel-staging case. The highest staging ratio gives rise to the most homogeneous profile among the three cases considered. The explanation resembles the one given to explain the lower inhomogeneity found for  $\phi = 0.85$ : a higher amount of unmixed fuel is introduced in the system resulting in a higher share of unreacted fuel and reactive radicals, which are then available to continue the reaction in the other combustion zones. Finally, an increased swirl number exhibits a higher value of the inhomogeneity factor with respect to the standard operating point.



## 4 Oxyfuel Combustor

As already outlined in the introduction chapter, combustion of fossil fuels dominates the global energy market, and will continue to dominate it in the future, as just a slight decrease is forecasted in the next decades [1]. The use of fossil fuels to feed combustion-based devices has a strong environmental impact that now more than ever must be minimized. The challenge of combustion research is to explore new ways to reduce pollutant emissions along with high process efficiency. One option lies in a continuous improvement of the combustion system or the application of new combustion concepts [3], such as oxyfuel combustion. In this concept, air is replaced by a mixture of carbon dioxide ( $\text{CO}_2$ ) and oxygen as oxidizer, leading to an exhaust gas mainly composed of  $\text{CO}_2$  and water vapor. The  $\text{CO}_2$  can be separated, liquefied and stored underground to reduce the effects on the environment [3].

The need to understand the impact of a different boundary condition on the combustion process, in order to optimise combustion-based devices, states the importance of this chapter: it is dedicated to the CRN modelling of an intermediate-scale (20 kW) combustor designed at Technische Universität Darmstadt, suitable for operating gas flames as well as gas-assisted coal flames, exploring both air and oxyfuel atmospheres. The modelling is aided by RTD data [69], [70] already available for this test-rig. As highlighted in paragraph 2.3, such a modelling proves its strength when investigating new combustion concepts: RTD-derived CRN models are a powerful candidate for a first examination on the impact of the operating conditions with respect to the benchmark combustion process in terms of simple mixing and reaction zones. After the description of the experimental apparatus, the CRNs are retrieved and explained based on previous experimental evidence. The network is sized against RTD data, and, for the reactive case, a comparison between the calculated emissions and the measured ones is carried out. The good agreement that stems from this comparison gives confidence about the retrieved model, that is subsequently used to gain insight into the mixing and reactive features of the combustor operating in air and oxyfuel atmospheres.

The goal of this chapter is to exploit the reactor models to identify and discuss the effect of the oxidizer (namely air or oxyfuel) on the mixing and reactive features of the flow.

### 4.1 Experimental apparatus

The test rig under investigation is an intermediate-scale combustor, suitable for operating gas flames as well as gas-assisted coal flames. It is designed to close the gap between unconfined laboratory-scale coal burners and confined industrial-scale coal combustors and allows the exploration of both air and oxyfuel atmospheres. In the following, it is referred to as OFC (OxyFuel Combustor). Thorough experimental investigations have been carried out in this apparatus [69], [70], [117], [118], [136], supported as well by numerical simulations [137], [138]. Figure 78 shows the geometry. Dimensions are provided in Table 24. The burner down-fires into the combustion chamber. Walls are made of wedged fused silica to enable optical access. Inside the burner quarl, two inlet orifices surround a bluff body (magnification in Figure 78.b): a partially premixed mixture of fuel and oxidizer (air or oxyfuel, details in Table 24) is exiting the inner orifice (primary flow, FI), whereas swirled oxidizer issues through the outer orifice (secondary flow, FII). A tertiary flow, FIII, of oxidizer is injected close to the windows (Figure 78.a). In the following, the cases employing air as diluent of the system are addressed as NRair (non-reactive) and Rair (reactive), whereas, when using an oxyfuel mixture, the cases are added as NR30 and R30. Details about the characteristics of the two operating points explored are reported in Table 24.

RTD measurements have been carried out both in non-reactive and reactive conditions [69], [70]. The operating points are listed in Table 24. For non-reactive measurements,  $\text{CH}_4$  was injected as a gaseous tracer in the primary flow orifice (see Figure 78) and was detected in-situ by means of direct Tunable Diode Laser Absorption Spectroscopy (TDLAS). The gas phase RTD was measured probing the concentration of  $\text{CH}_4$  injected in the primary flow at the inlet and representative positions at the

combustor exit simultaneously, using a diode laser. It was shown that the choice of the tracer had a negligible impact on the flow and the measured tracer response. HCl was instead chosen as a tracer to measure the RTD during combustion.

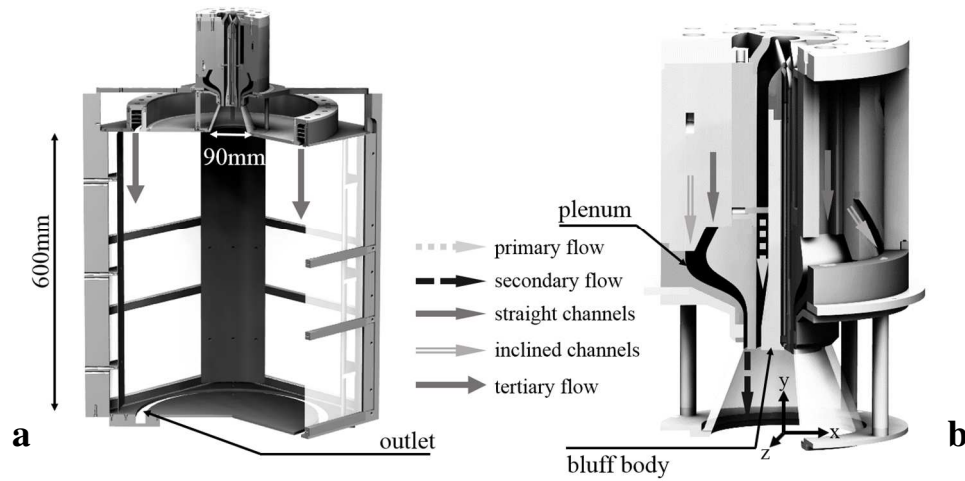


Figure 78: Sectional view of the oxyfuel combustor. (a) Complete combustion chamber; (b) magnification of the burner region.

Table 24 : relevant dimensions of the combustion chamber and details of the points of operation [117].

Quarl dimensions	[mm]	Operation points	NRair / Rair	NR30 / R30
Larger diameter, D	90	Oxidizer Air/O <sub>2</sub> /CO <sub>2</sub> (vol%)	100/0/0	0/30/70
Smaller diameter, d	49.2	I CH <sub>4</sub> (m <sup>3</sup> /h)	2.01 (only for Rair)	2.01 (only for R30)
Height	53	I Oxidizer (m <sup>3</sup> /h)	13.55	8.16
<b>Combustion chamber dimensions</b>	[mm]	II Straight Oxidizer (m <sup>3</sup> /h)	5.97	3.76
Length	600	II Inclined Oxidizer (m <sup>3</sup> /h)	12.02	7.27
Width	420	III Oxidizer (m <sup>3</sup> /h)	69.95	42.60
Depth	420			

## 4.2 Chemical Reactor Network

The data from the RTD measurements carried out in [70] are employed to fit a network of interconnected ideal flow reactors. Two operating conditions, concerning different operating atmospheres, are explored, both for non-reactive and reactive flow, Table 24. In the following paragraph, the designed CRNs are introduced and the choice of the reactor arrangement is discussed based on the available experimental data of the combustor. Afterwards, the experimental fit is shown, together with a quantification of the numerical error. For the reactive case, a comparison between the kinetic output of the network and experimental data [136] is also carried out.

### 4.2.1 Non-reactive flow

Figure 79 guides the design of the CRN, shown in Figure 80 and Figure 81, based on zonal modelling of the flow. Figure 79.a shows the flow field of the non-reactive operation points [117], considering the quarl region (upper row), and a small part of the combustor at the exit of the quarl; while Figure 79.b shows flow streamlines of the entire combustor flow field, calculated for NRair [137], comprising a schematization that highlights the main mixing zones [137]. In the quarl zone, Figure 79.a, a small corner



recirculation is present at the entrance of the inlet streams, not reproduced in Figure 79.b. The flow continues its path forming a lateral jet-like region, where segregated flow streamlines can be assumed, and a central IRZ, that recirculates flow from the jet region. Both identified flow features, the jet region and the IRZ, continue further downstream the dump plane of the quarl. According to Figure 79.b, after the ensemble “jet-IRZ”, follows a segregated region, that serves as post-flame zone under reactive conditions. After the quarl zone, there is introduction of oxidizer by means of the lateral inlets. They define a “dilution region”, creating lateral recirculation zones. A mixed exit region is identified before the exit of the combustor. Given the symmetry of the system, a 2D model is adopted. Figure 80 and Figure 81 propose a simple schematization of the flow field.

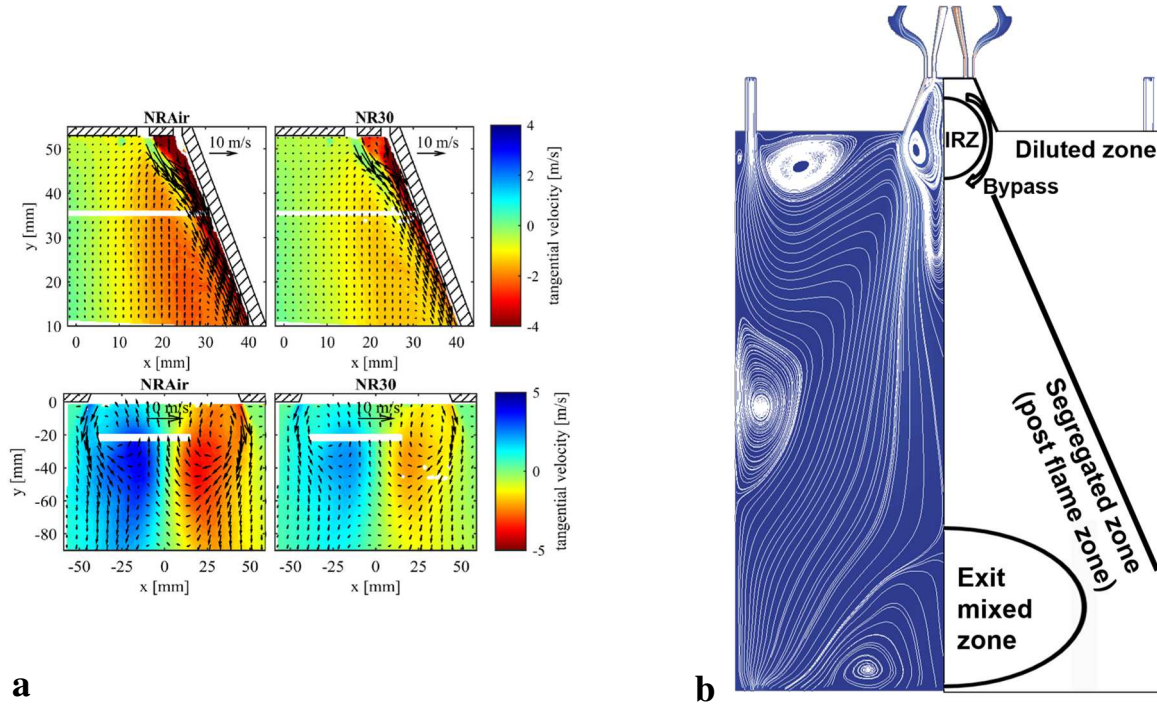


Figure 79: **a**, flow field of non-reactive operation points [117]; **b**, CFD calculation of the mean flow field for NRAir, comprising a schematization highlighting the main mixing zones [137].

Figure 80 shows the CRN of the near-burner region of the OFC. It comprises the portion shown in Figure 79.a, equivalent to the bypass-IRZ part in Figure 79.b. As for the previous case, in paragraph 3.3.1, a PFR is adopted to schematize the bypass region, characterized by strong preferential direction of the flow. The corner RZ and the IRZ are regarded as mixed zones. After this entrance zone, a plug flow zone is identified until a final mixing zone. The dilution region is modelled as a series of PFRs in parallel with CSTRs, exemplifying the vortex-zones clear from Figure 79.b.

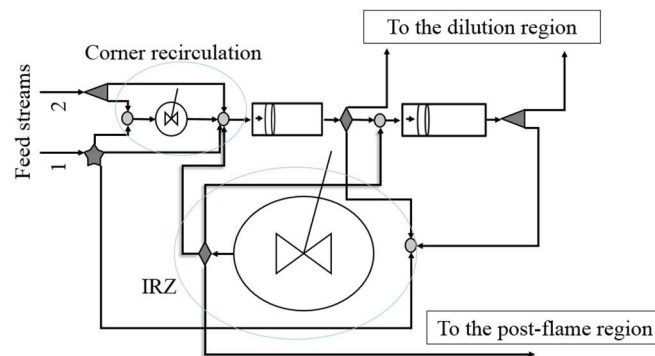


Figure 80: CRN of the near-burner region of the OFC. It comprises the portion shown in Figure 79.a, equivalent to the bypass-IRZ part in Figure 79.b.

The parameters to be optimized are the splitting ratios and the volumes of the near wall mixed zones identified in the dilution region in Figure 79.b. As explained in 2.2.1, the mathematical model describing

the mixing behaviour of the network is implemented in Matlab®, and the network superstructure reproduced in Simulink®. An optimization routine is applied to retrieve the network parameters by means of the minimization of an objective function (more in paragraph 2.2.1 and paragraph 3.3.1, Equation 37).

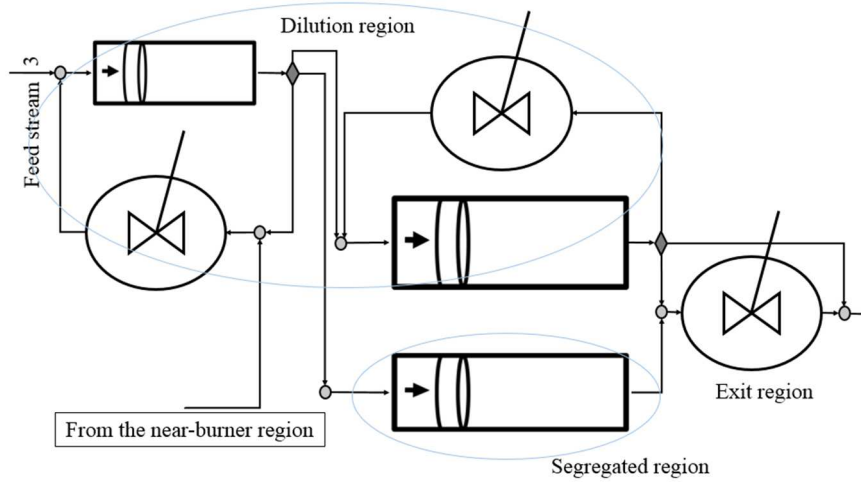


Figure 81: schematization of the combustor without the near burner region, Figure 80. The CM shown here comprises the segregated zone, the dilution zone and the exit zone in Figure 79.b.

#### 4.2.1.1 Experimental fit

Figure 82 shows the dynamic response of the CRN after the parameter estimation via the optimization routine. It is superimposed to the experimental curve, and the residuals between the experimental tracer response and the CRN optimized response are reported. The Inlet Pulse is shown for graphical comparison, though scaled to the maximum of the plots for graphical reasons.

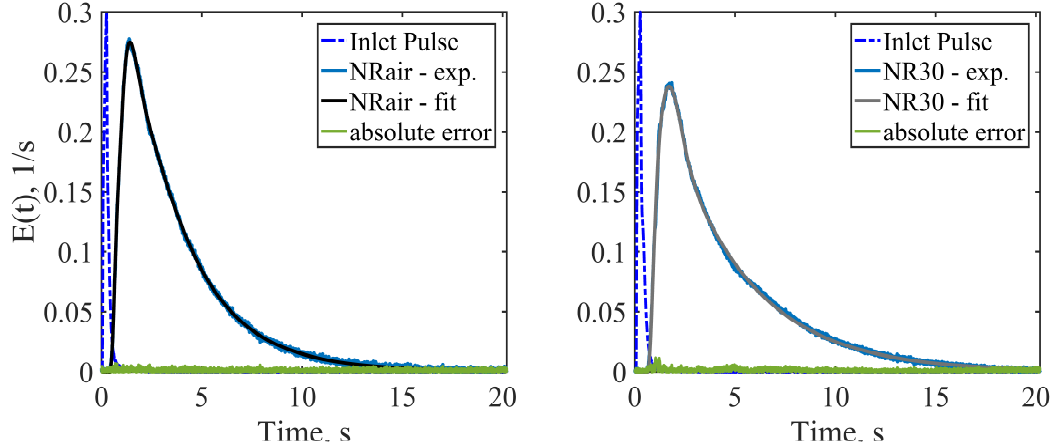


Figure 82: experimental RTD with superimposed CRN fit, NRair and NR30.

Figure 83 and Table 26 quantify the uncertainty of selected RTD parameters. The parameters used to carry out the comparison are defined below, in Table 25.

Table 25: parameters used to carry out the comparison between the operating atmospheres.

Parameter	Explanation		NRair – average fit
$\tau_1^m$	Mean residence time inside the system.	$\tau_1^c$	Convective time delay, time before the first arrival of the tracer.
$\sigma_1^2$	Variance of the distribution.	$\tau_i^{0.95}, \tau_i^{0.99}$	Time necessary for the 95% or the 99% of the tracer to exit the system.
$S_1^3$	Skewness of the distribution	$\frac{m_{IRZ}}{m_{in\_quarl}}$	Mass flow entrained into the IRZ, related to the mass flow fed to the quarl.
$\frac{m_{main \rightarrow dilution}}{m_{total\_feed}}$	Amount of mass flow from the main flow region to the dilution region, related to the total mass flow fed to the system	$\tau_{IRZ}$	Mean residence time in the IRZ
$\frac{m_{dilution \rightarrow main}}{m_{total\_feed}}$	Amount of mass flow from the dilution region to the main flow region, related to the total mass flow fed to the system	$\frac{\tau_{dead}}{\tau^m}$	Residence time associated to dead zones in the system, related to the mean residence time inside the system.
$\frac{V_{dead}}{V_{tot}}$	Volume associated to dead zones in the system, related to the total volume of the system.		

Beside the main moments of the distribution (explained in paragraph 2.2), few network-derived parameters are proposed that are chosen to carry out the comparison between the different operating conditions in the following paragraph 4.3.1.

As in section 3.3.1.1, the uncertainty was calculated fitting the network to the single-injection data. In this case, the experimental RTD was averaged from 50 single-injection curves. The proposed calculation considers only ten curves from this dataset, and NRair was chosen to carry out the analysis. Therefore, Figure 83 compares the fit of the average RTD, the one shown in Figure 82, with the single-injection fits. The standard deviation among the ten fits of the single injections is included.

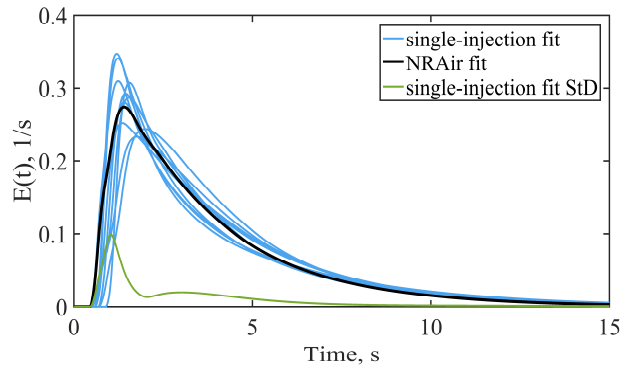


Figure 83: comparison among the fit of the average RTD and the fits of the single injection curves. The standard deviation among the ten single-injection fits is also proposed.

Table 26 reports the standard deviation among the ten single-injection fits. The parameters obtained from the fit of the average RTD (NRair in Figure 82) and the mean of the values of the same parameters calculated for each single injection (column “Mean values”) is also compared. Globally, the mean value of the parameter coincides or is close (in the calculated error) to the one calculated for the average fit. Larger errors are attributed to the use of 10 single-injections instead of 50.

Table 26: uncertainties associated with the CRN fit, NRair

	NRair – average fit	Mean values		NRair – average fit	Mean values
$\tau_1^m$	$3.8 \pm 0.2$	4.0	$\tau_1^c$	$0.4 \pm 0.1$	0.6
$\sigma_1^2$	$8.09 \pm 1$	9	$\tau_1^{0.95}$	$9.6 \pm 0.5$	10.3
$S_1^3$	$1.75 \pm 0.09$	1.71	$\tau_1^{0.99}$	$14.1 \pm 0.7$	14.8
$m_{main \rightarrow dilution}$	$0.21 \pm 0.04$	0.22	$m_{IRZ}$	$1.4 \pm 0.2$	1.6
$m_{total\_feed}$			$m_{in\_quarl}$		
$m_{dilution \rightarrow main}$	$0.79 \pm 0.07$	0.84	$\tau_{IRZ}$	$0.076 \pm 0.006$	0.067
$m_{total\_feed}$					
$\frac{V_{dead}}{V_{tot}}$	$0.33 \pm 0.03$	0.35	$\frac{\tau_{dead}}{\tau^m}$	$0.5 \pm 0.1$	0.6

In addition to the provided error analysis, a sensitivity analysis as the one shown in paragraph 3.3.1.2 is also carried out. It is in this case restricted to the mixing characteristics of the reactors of the network, as the choice of the interconnected macromixing zones is a crucial point in CRN research. The aim is to assess the relevancy of this choice and comment on its effect on the overall fit quality. The model shown in Figure 80 and Figure 81, after fitting to the experimental curve, is run in one case on a network comprising only CSTR reactors and in the other case on a network comprising PFR reactors only. The result is shown in Figure 84. Figure 84.a concerns the result for NRair, and Figure 84.b shows the one for NR30.

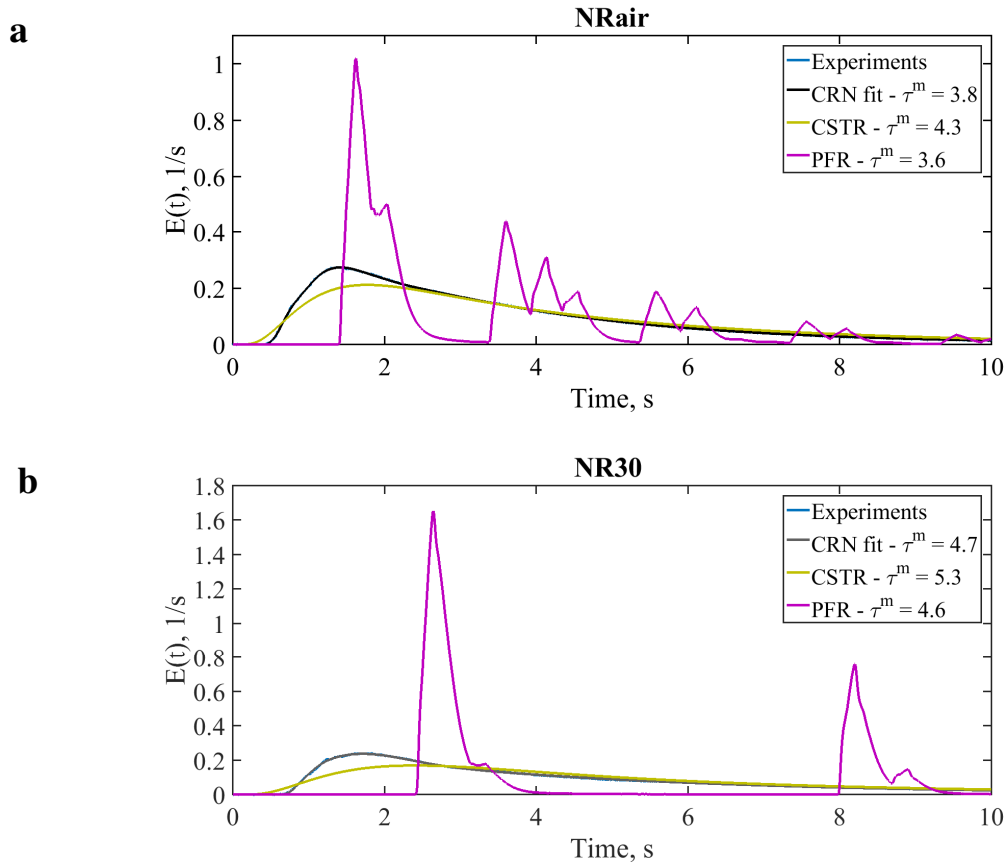


Figure 84: effect of the mixing characteristics of the reactors on the optimized response curve. (a) Results for NRair; (b) results for NR30.

The most noticeable impact on the response of the CRN is achieved for both operating conditions when swapping mixed zones for segregated ones, resulting in a network of interconnected PFRs. In this case,

not only the onset of the curve is heavily delayed, but its shape exhibits distinct peaks with decreasing intensity, closely resembling the behaviour of one PFR with recycle depicted in [36]. A network comprising just CSTR reactors shows an earlier rise of the RTD with respect to the experimental response, and a broader distribution as confirmed from the larger calculated  $\tau^m$  both for NRair and NR30. This effect is expected, because replacing plug-flow zone with mixing zone corresponds to removing the zones that are responsible for a delay in the response of the system, explaining the earlier onset of the distribution. Nonetheless, the CSTR-curve in Figure 84 is the one that shows a closer resemblance to the original curve, meaning that the mixed zones in the system play a major role in determining its response. The explanation for the extremely different behaviour of the PFR-curve is attributed mainly to the presence of dead zones, that are normally represented by a CSTR. These zones exhibit a high mean residence time when compared to those of the other zones. Therefore, when these zones are regarded to as plug-flow zones their mean residence time becomes a delay time, heavily delaying the streams trapped in the recycle loop. Another reason for the extremely different behaviour lies in the mixing characteristics of the outlet zone in Figure 81, which, according to Figure 79.b, is schematized as a CSTR. The exit zone plays a crucial role in the final broadening of the response, feature that is missing for the PFR-curve.

A last comment concerns the major impact observed for the OFC while changing the reactors type with respect to the SSGT, described in paragraph 3.3.1.2. For the SSGT the effect of the different reactors type on the response curve is apparently less pronounce because of the severe broadening effect induced by the pre-combustor path, addressed in section 3.3.1.3 for the cold flow. The tracer response of the OFC is not affected by such a phenomenon, as discussed in the section below,

#### 4.2.1.2 RTD extraction from tracer responses

Once the network was calibrated against the measured tracer response, the response of the system was calculated using as input signal an ideal numerical pulse, instead of the experimental one. As in 3.3.1.1, the aim was to check whether it was more appropriate to employ distributions generated by an ideal signal in order to properly describe the observed phenomena. As shown in Figure 85, the experimental pulse gives rise to a distribution that is very close to the one generated by an ideal pulse. Differently from the SSGT, the tracer response and the RTD coincide in this case. As shown in both Figure 82 and Figure 85, the experimental pulse is sharp compared to the subsequent distribution, fulfilling the condition for an appropriate pulse input to be far shorter than the mean residence time in the system. Furthermore, the amount of dispersion between injection point and reactor entrance must be negligible. These conditions are satisfied by the present experiment [70]. Therefore, the tracer response directly yields the  $E(t)$  of the combustor. For this reason, it will be employed in the following discussion without further processing.

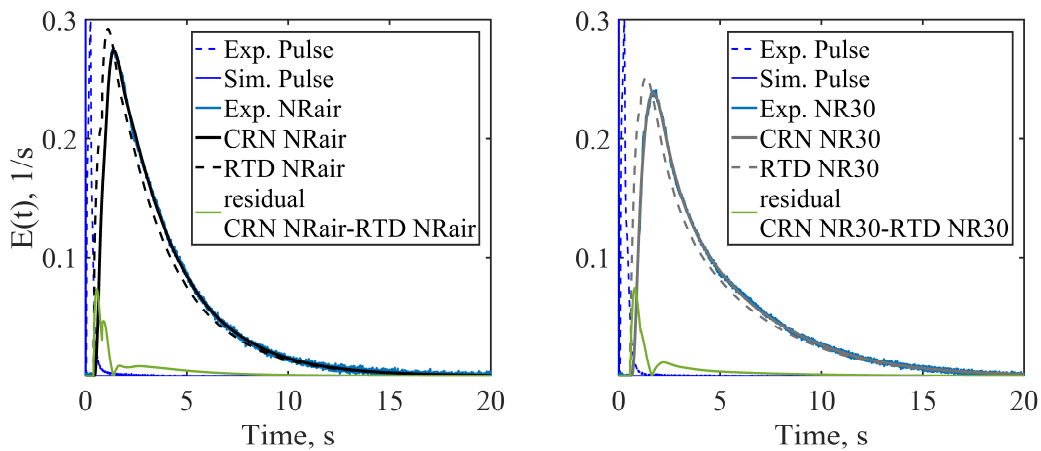


Figure 85: experimental RTD with superimposed CRN fit, NRair and NR30.

## 4.2.2 Reactive flow

The CRN designed to model the reactive flow exhibits a slight modification with respect to the one presented in 4.2.1. As for the SSGT case, par. 3.3.2, an additional zone was added, splitting the IRZ volume. This additional zone has the aim of representing, even if by means of a gross schematization, a high temperature region approximately schematizing the flame zone, Figure 86. Only the modified near-burner region is shown.

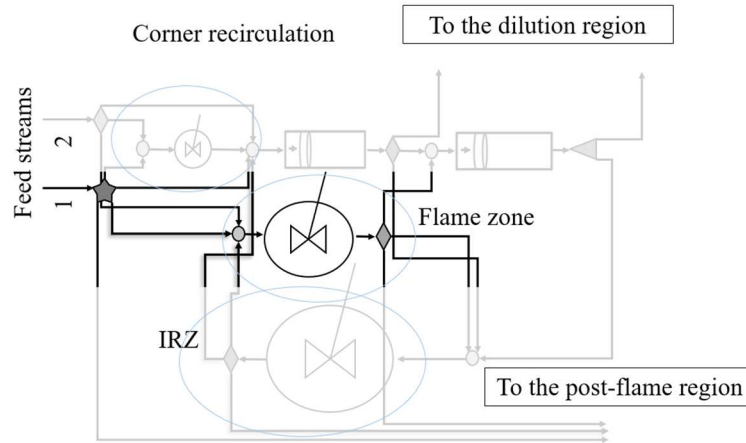


Figure 86: modification to the near-burner region (Figure 80) to take chemical reaction into account.

Indeed, par. 1.2, swirling flows encourage the stabilization of the flame in the shear layers delimiting recirculation zones. Given the existence of a zone yielding high temperatures and high species formation rate, it is incorrect to not take it into account while examining the reactive case. Therefore, a zone referred to as “flame zone” is added to the CRN, in the near burner region. It is represented by a CSTR, due to the high turbulence levels and the mixing associated with the swirl motion. The rest of the CRN remains the same, and it is based on the flow features discussed in 4.2.1. An important characteristic of reactive swirling flows is the reduction of the size of the internal recirculation zone due to the higher flow momentum, with respect to non-reactive flow [123]. As the definition of the CRN volumes is crucial, as stated also in [68], Figure 87 aided the sizing of the zones for reactive conditions.

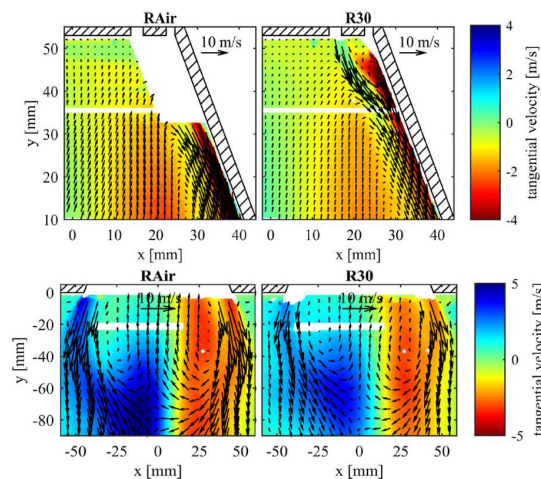


Figure 87: flow field of reactive operation points [117].

### 4.2.2.1 Experimental fit

Figure 88 shows the dynamic response of the CRN after the parameter estimation via the optimization routine. It is superimposed to the experimental curve, and the residuals between the experimental tracer



response and the CRN optimized response are reported. The Inlet Pulse is shown for graphical comparison, though scaled to the maximum of the plots for graphical reasons.

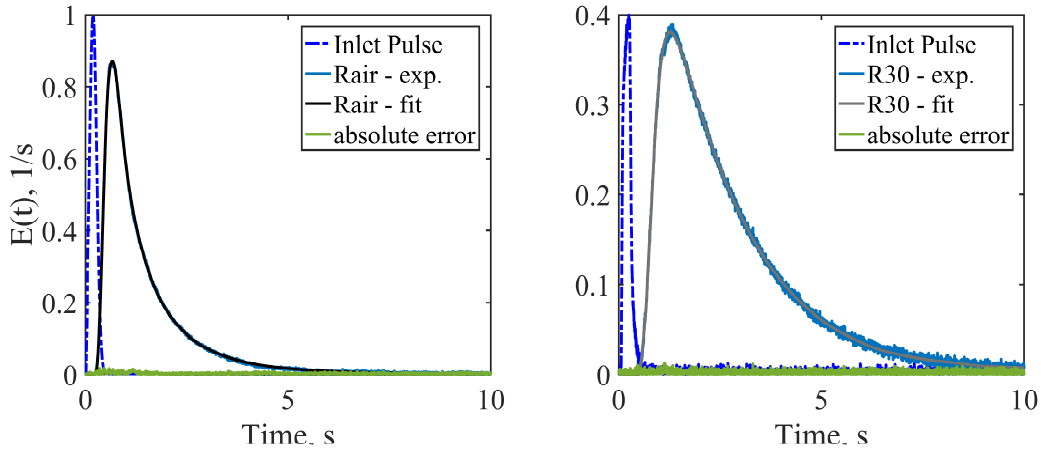


Figure 88: experimental RTD with superimposed CRN fit, Rair (left) and R30 (right).

Table 27 contains the uncertainties associated to selected fit-derived parameters. These parameters are chosen to carry out the comparison on the impact of the oxidizer on the flow and reacting field, 4.3.2.

Table 27: uncertainties associated with the CRN fit, Rair

	Rair – average fit	Mean values		Rair – average fit	Mean values
$\tau_1^m$	$1.5 \pm 0.2$	1.6	$\tau_1^c$	$0.25 \pm 0.05$	0.26
$\sigma_1^2$	$1.7 \pm 0.5$	1.6	$\tau_1^{0.95}$	$4.1 \pm 0.5$	4.0
$S_1^3$	$2.8 \pm 0.2$	2.8	$\tau_1^{0.99}$	$7 \pm 1$	7
$m_{main \rightarrow dilution}$	$0.21 \pm 0.04$	0.22	$m_{IRZ}$	$0.50 \pm 0.09$	0.55
$m_{total\_feed}$			$m_{in\_quarl}$		
$m_{dilution \rightarrow main}$	$0.54 \pm 0.09$	0.62	$\tau_{IRZ}$	$0.026 \pm 0.004$	0.022
$m_{total\_feed}$			$m_{flame}$	$0.4 \pm 0.1$	0.3
$m_{dead}$	$0.8 \pm 0.1$	0.8	$m_{in\_quarl}$		
$m_{tot}$			$\tau_{flame}$	$0.002 \pm 0.002$	0.003
$V_{dead}$	$0.31 \pm 0.05$	0.31			
$V_{tot}$					

As in the previous paragraph, 4.2.1, uncertainty was calculated fitting the network to ten single injections measured distribution curves out of fifty. Rair was chosen to carry out the analysis. Figure 89 compares the fit of the average RTD (Figure 88) and the fits of the ten considered single injection curves. The standard deviation among the ten single-injection fits is also proposed.

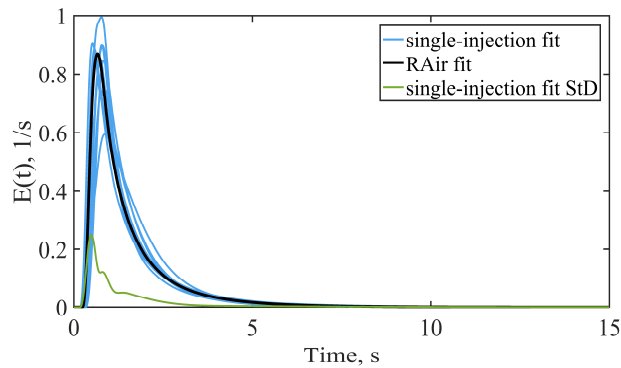


Figure 89: comparison among the fit of the average RTD and the fits of the single injection curves. The standard deviation among the ten single-injection fits is also proposed.

Beside the good CRN calibration against the measured RTD data, which shows that the designed model has the potential to properly describe the mixing features inside the system, a comparison between the CRN emission prediction and available experimental evidence on species concentration [136] is also carried out to comment on the suitability of the model to capture also the chemical reaction properties of the system. This assessment is shown in Table 28, where species concentrations calculated from the CRN after optimization are compared with experimental data collected 35 mm above the exit plane of the combustor. This measurement location is taken as comparison because it is easily recognized as belonging to a determined reactor-zone inside the combustor, namely the mixed exit zone (see Figure 79.b and Figure 81).

Table 28: comparison between experimental data [136] and CRN-predicted species concentration near the exit of the combustor.

	CO, ppm		CO <sub>2</sub> , mole fraction		H <sub>2</sub> O, mole fraction		CH <sub>4</sub> , ppm	
	CRN	Exp.	CRN	Exp.	CRN	Exp.	CRN	Exp.
Rair	1140	1300	$1.90 \times 10^{-2}$	$1.9 \times 10^{-2}$	$4 \times 10^{-2}$	$3.9 \times 10^{-2}$	559	570
R30	107	~ 40	$7.1 \times 10^{-1}$	$7.25 \times 10^{-1}$	$6.2 \times 10^{-2}$	$6.1 \times 10^{-2}$	61	< 60
	O <sub>2</sub> , mole fraction							
	CRN	Exp.						
Rair	$1.6 \times 10^{-1}$	$1.7 \times 10^{-1}$						
R30	$2.3 \times 10^{-1}$	$2.2 \times 10^{-1}$						

The GRI 3 kinetic mechanism was used to carry out this analysis because the complete C1 – C4 mechanism was not reaching convergence. The chance of this issue happening has been pointed out before, paragraph 3.3.2.3. Owing to the similar prediction shown in paragraph 3.3.2.3, the GRI 3 mechanism has been employed in the following to calculate species formation in the OFC.

The agreement is good for Rair, for all the species considered. R30 shows an overall good agreement for all the species except CO. In this case, the model overestimates its value, and this overestimation is mirrored by the lower CO<sub>2</sub> mole fraction value. CO is one of the species with the highest sensitivity to the flow field characteristics. It is possible that the present model, even if properly calibrated in order to catch all the main mixing features, slightly overestimates the mixing with the dilution region. This region has a low temperature compared with that of the main flow path, and, as shown in par. 4.3.2, its CO content is high because of the quenching of the reactions at low temperatures. If a higher share of reacting flow carrying CO is entrained in the cold side zone, a higher amount of CO will be quenched and available for mixing along the combustor coordinate. Despite this discrepancy, the overall suitability of the model to reproduce the RTD and the reactive features of the combustion chamber has been proven: there is indeed a higher CO prediction for R30, but the significant CO reduction compared to Rair is correctly reproduced. The model is therefore employed in 4.3.2 to draw conclusion on the behaviour of the system while changing the oxidizer.

## 4.3 Results and discussion

In the following, the impact of the operating atmosphere on the behaviour of the OFC is retrieved. First, the effect on the cold flow is described, par. 4.3.1, followed by comments on the reactive flow as well, par. 4.3.2.

### 4.3.1 Non-reactive flow – effect of the oxidizer

The RTDs retrieved by means of the CRN fit are shown superimposed to each other in Figure 90, to describe the mixing behaviour of the combustor while operating under different atmospheres. The main three moments of the distributions are reported in Table 29. Selected flow parameters are reported as well, to aid the description of the results.



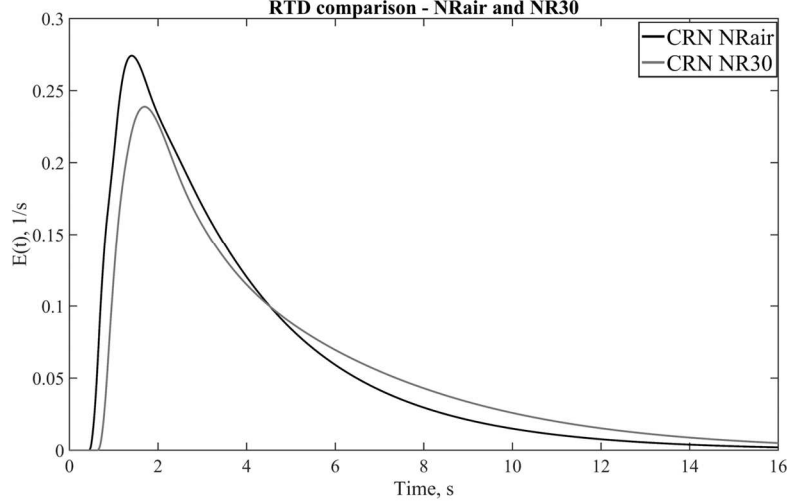


Figure 90: comparison between the CRN fit for NRair and NR30.

From Figure 90, the NR30 appears delayed with respect to NRair, and generates a broader distribution of residence times. Accordingly, the value of the calculated  $\tau^m$  is larger for oxyfuel atmospheres. These features agree with the lower mass flow rate fed to the system in this case, Table 24. Therefore, a lower bulk velocity is associated with NR30, justifying the delayed arrival of the tracer to the detection point. The lower bulk velocity, also meaning a lower impulse of the flow entering the combustion chamber, is also responsible for a greater share of the combustor volume associated to the IRZ, as can be seen also from Figure 79.a. Here, the zone identified as IRZ is the one where the velocity vectors exhibit a smaller value of the velocity magnitude and no preferential flow direction is identified. For NRair, the velocity vectors around the mixing zones indicate a larger velocity magnitude with respect to NR30, and the volume percentage of the recirculation zone appears as well to be higher, in agreement with the findings from [123]. In this recirculation zone, more mass flow is entrained for the oxyfuel atmosphere with respect to the mass flow fed to the quarl zone,  $\frac{m_{IRZ}}{m_{in\_quarl}}$ . This effect is balanced by the larger IRZ volume, resulting in a higher value of the recirculation time in this zone,  $\tau_{IRZ}$ .

Table 29: global properties of the RTDs and CRN-fit parameters, NRair and NR30

	NRair	NR30		NRair	NR30
$\tau_1^m$	3.8	4.7	$\tau_1^c$	0.4	0.7
$\sigma_1^2$	8	12	$\tau_1^{0.95}$	9.6	11.9
$S_1^3$	1.75	1.48	$\tau_1^{0.99}$	14.1	16.5
$\frac{m_{main \rightarrow dilution}}{m_{total\_feed}}$	0.21	0.17	$\frac{m_{IRZ}}{m_{in\_quarl}}$	1.4	1.6
$\frac{m_{dilution \rightarrow main}}{m_{total\_feed}}$	0.79	0.85	$\tau_{IRZ}$	0.077	0.084
$\frac{V_{dead}}{V_{tot}}$	0.33	0.30	$\frac{\tau_{dead}}{\tau^m}$	0.4	0.6

The amount of mass flow exchanged between main flow path and the dilution zone with respect to the total mass flow fed to the combustor,  $\frac{m_{main \rightarrow dilution}}{m_{total\_feed}}$ , is slightly higher for NRair. On the other hand, the amount of mass flow exchanged between the dilution zone and the main flow path,  $\frac{m_{dilution \rightarrow main}}{m_{total\_feed}}$ , is higher for oxyfuel atmospheres. This is likely an explanation for the longer oxyfuel distribution: the recirculation zones identified in the dilution region of the combustor (clear from Figure 79.b) present the largest residence times in the system and are therefore regarded as dead volume zones. This is in agreement with observations from [69]. As these dead zones cause longer local residence times, the

mass flow from these zones has experienced a high mixing time, and its tracer concentration is severely broadened. A higher percentage of this heavily mixed flow is then transported into the main flow for NR30, causing the stretch of the tail of the oxyfuel distribution. The ratio of the dead time to the mean residence time,  $\frac{\tau_{dead}}{\tau^m}$ , corroborates this hypothesis.

### 4.3.2 Reactive flow – effect of the diluent

The RTD-fits obtained after optimizing the parameters of the reactive CRN for both operating atmospheres are compared in Figure 91. Table 30 contains the value of the three principal moments of the RTDs and selected parameters chosen to aid the comparison between the two operating conditions. What clearly emerges is the huge difference between the spread of the two distributions, and the strong resemblance between R30 and NR30 (shown in Figure 90). Referring to Figure 90, the maximum value of the distribution corresponding to NR30 is around  $0.25 \text{ s}^{-1}$ ; and the one corresponding to R30 is around 0.4 (Figure 91). Instead, the two maxima corresponding to NRair (around 0.275) and Rair (around 0.9) are distant from each other, as expected when comparing a cold flow distribution to a reactive flow one (higher temperatures). The broadening of the R30 distribution is the cause of the higher  $\tau_1^m$  and  $\sigma_1^2$ , Table 30.

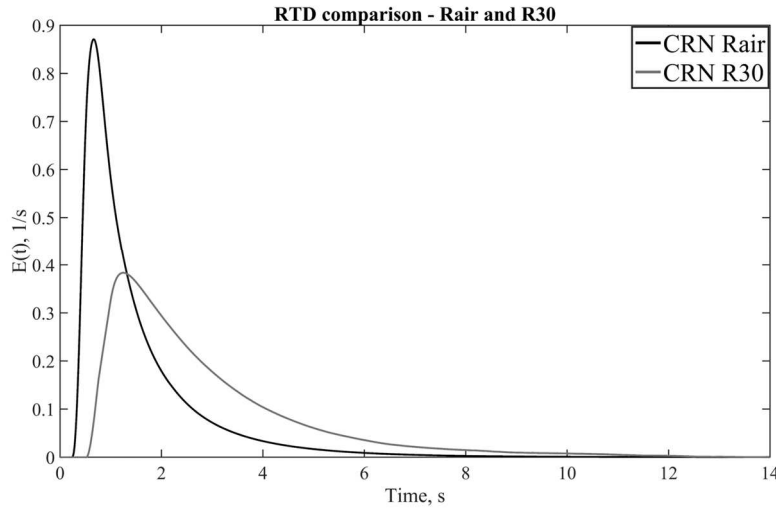


Figure 91: comparison between the CRN fit for Rair and R30.

The first cause for the broader distribution found for R30 is the lower mass flow introduced into the system in this case, compared to Rair. For this reason, higher residence times are associated with the oxyfuel atmosphere, despite the higher measured temperatures [136] that should translate to a faster flow [123] by virtue of the thermal expansion. In addition to the lower amount of mass fed to the system, a higher entrainment in recirculation zones has been calculated from the model for R30. The parameter  $\frac{m_{IRZ}}{m_{in\_quarl}}$  is approximately one order of magnitude higher when feeding the  $O_2/CO_2$  as oxidizer, while the amount of mass flow entrained in the lateral recirculation zones,  $\frac{m_{V_{dead}}}{m_{total\_feed}}$ , is nearly doubled. Therefore, a higher share of the flow experiences strong mixing inside the system, broadening the distribution. The parameters  $\frac{m_{main \rightarrow dilution}}{m_{total\_feed}}$  and  $\frac{m_{dilution \rightarrow main}}{m_{total\_feed}}$  present similar values in both cases, differently from the non-reactive case.

Table 30: global properties of the RTDs and CRN-fit parameters, Rair and R30

	Rair	R30		Rair	R30
$\tau_1^m$	1.5	2.9	$\tau_1^c$	0.25	0.52
$\sigma_1^2$	1.7	3.8	$\tau_1^{0.95}$	4.1	7.0
$S_1^3$	2.8	1.9	$\tau_1^{0.99}$	7	10
$m_{main \rightarrow dilution}$	0.21	0.23	$m_{IRZ}$	0.50	1.38
$m_{total\_feed}$			$m_{in\_quarl}$		
$m_{dilution \rightarrow main}$	0.54	0.50	$\tau_{IRZ}$	0.026	0.012
$m_{total\_feed}$			$m_{flame}$	0.4	0.6
$\frac{V_{dead}}{V_{tot}}$	0.31	0.22	$m_{in\_quarl}$		
$\frac{V_{tot}}{m_{V_{dead}}}$	0.8	1.4	$\tau_{flame}$	0.002	0.002
$m_{total\_feed}$					

The impact on the kinetic behaviour of the system is addressed in the following, Figure 93. The coordinates refer to the coordinate system introduced in Figure 78.b, and the selected profiles are clarified below in Figure 92.

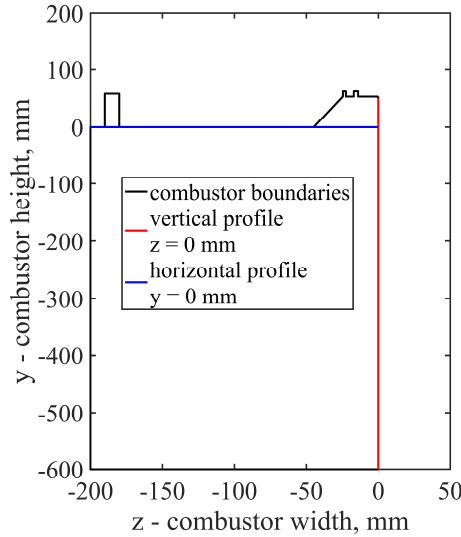


Figure 92: sketch of the lower half of the OFC. The horizontal (blue) and vertical (red) profiles used to show species formation under different operating conditions are highlighted.

The vertical profile in Figure 93 is taken along a central vertical line passing through the combustor starting from the inlet of the quarl until the exit plane (red line in Figure 92). The horizontal profile follows a line cutting the combustor horizontally just below the exit of the quarl (blue line in Figure 92). In Figure 93, the upper row shows the temperature along the vertical centreline of the combustor (right side) and the horizontal line at the dump plane of the quarl (left side), the middle row presents the  $CO$  mole fraction, followed by the methane mole fraction in the third row and the oxygen mole fraction in the lower row. Starting the description from the vertical profile (panels on the left in Figure 93), the first, flat part of all shown quantities (temperature,  $CO$  mole fraction,  $CH_4$  mass fraction  $O_2$ ) corresponds to the identified IRZ. Follows the PFR post-flame region, and the last flat part representing the exit stirred region. The CRN fit temperatures (Figure 93, vertical profile, upper row) do not significantly differ in the IRZ, and their value is around 1800 K for both atmospheres. The  $CO$  mole fraction in this region is higher for R30, but the intense mixing and reaction encouraged by the IRZ is clear: the values are below 500 ppm, and no methane is present in this zone. In the post-flame region, the behaviour is similar at the beginning, though yielding different concentration values, and then differs for the two examined cases. More in detail, for Rair the  $CO$  concentration experiences a sharp rise, due to the combined effect of direct transport of flow from the reaction regions and from the side dilution region (the coordinates that identify the dilution region range roughly from  $z = -50$  to  $z = -200$  in Figure 93, horizontal

profile). The amount of carbon monoxide decreases until the temperatures are high enough to promote the reactions ( $> 1000$  K), and then increases again as the low temperatures freeze the reactions and the CO that is formed is no longer oxidized to  $\text{CO}_2$ .

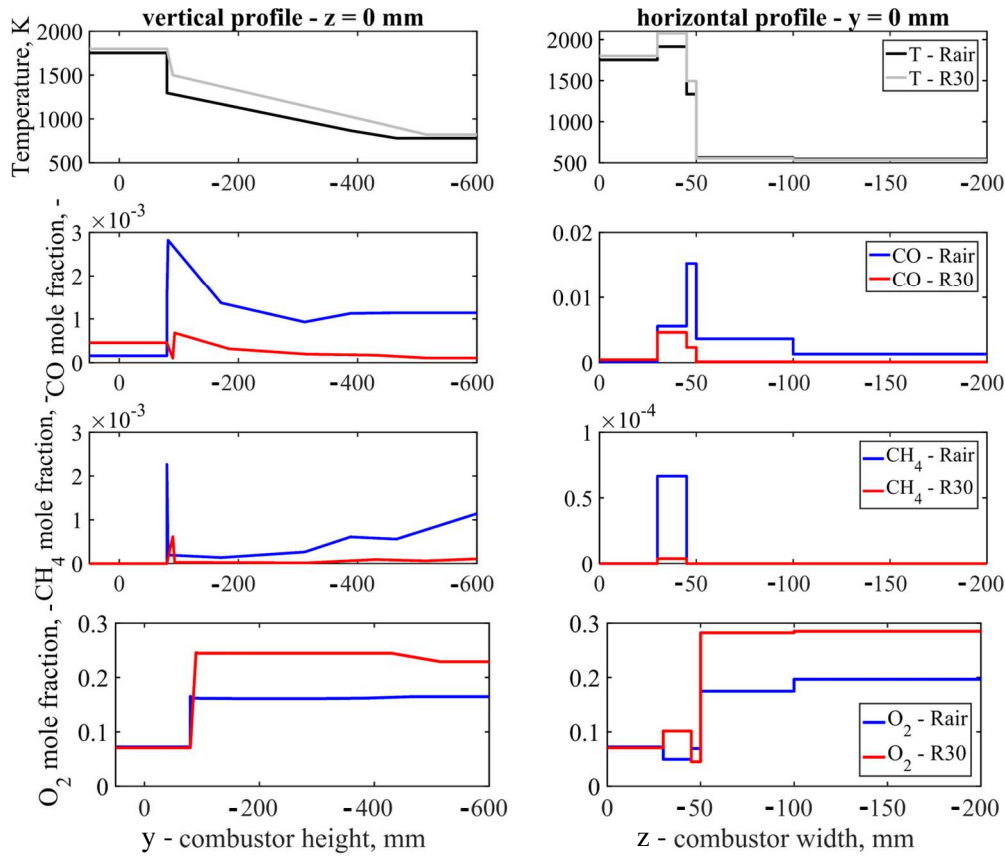


Figure 93: impact of the oxidizer on temperatures (CRN-fit) and species formation. Upper row: temperature along the vertical centreline of the combustor (right side) and the horizontal line at the dump plane of the quarl. Second row: CO mole fraction. Third row:  $\text{CH}_4$  mole fraction. Fourth row:  $\text{O}_2$  mole fraction.

R30 exhibits a slightly different situation: the CO content experiences as well an increase due to transport from CO-rich zones, but the intensity of this peak is approximately one order of magnitude lower than the one calculated for Rair, despite the higher fuel to oxidizer ratio that characterizes R30 (Table 24). This behaviour is attributed to several factors. The first one is the higher  $\frac{m_{\text{flame}}}{m_{\text{in, quarl}}}$  found for the oxyfuel atmosphere, Table 30: a higher share of the inlet mass flow is entrained in the high temperature CSTR used to simulate the flame region, meaning that less fresh fuel is available to react at a later stage in the system. Also, the higher temperatures enhance CO consumption, encouraging its reaction in the near-burner region (the near burner region is better visualized in Figure 93, horizontal profile,  $\sim -30 - -50$  mm). Furthermore, the model predicts a lower fuel-slip amount for R30, in accordance with [136], where the conclusion was based on species measurements. Due to the lack of reactive species and the slightly higher temperatures, the content of carbon monoxide decreases along the post-flame PFR, and decreases further in the exit region CSTR, owing to further mixing with the dilution mixture as well. It is worth to comment about the occurrence of fuel slip in the system. The model includes a flow split parameter that pushes flow from the quarl region to the post-flame region. This parameter is one order of magnitude lower for R30, meaning that the reaction consumes almost all the available reacting mixture. This is the explanation behind the different trend of the CO profile in the different operating conditions. The oxygen concentration is also reported. According to the vertical profile, the mixing and reaction lower its concentration in the IRZ, as expected in a reactive flow. After the reaction zone, the  $\text{O}_2$  concentration sharply increases again because of mixing of flow from the dilution region. From this point on, this

concentration remains rather constant for Rair and exhibits a slight decrease for R30, mainly attributed to the mixing from the side region.

The horizontal profile has partially already been introduced, to complement the observation of the phenomena along the vertical one. Its right part shows, once again, the species content in the IRZ. Then, the plot coordinate passes the reaction zone and the bypass (see Figure 80 and Figure 86). In the latter zone, there is a clear difference between Rair and R30: the CO and CH<sub>4</sub> content is significantly higher for Rair, meaning that the reaction is proceeding slower with respect to R30, whose CO and CH<sub>4</sub> content is significantly lower, because the reaction has already proceeded towards CO<sub>2</sub> formation. The oxygen content for Rair is lower as well, compared to the O<sub>2</sub> concentration calculated for the oxyfuel atmosphere.

In Table 31 the CRN-predicted species are shown against the species calculation calculated in the hypothesis of equilibrium. As for the SSGT (refer to paragraph 4.4), the equilibrium was calculated in the hypothesis of plug flow at constant temperature, set at 1500 K in this case.

Table 31: comparison between equilibrium calculations and CRN-predicted species concentration near the exit of the combustor.

	CO, ppm		CO <sub>2</sub> , mole fraction		H <sub>2</sub> O, mole fraction		CH <sub>4</sub> , ppm	
	CRN	Eq.	CRN	Eq.	CRN	Eq.	CRN	Eq.
Rair	1140	$2 \times 10^{-1}$	$1.90 \times 10^{-2}$	$1.97 \times 10^{-2}$	$4 \times 10^{-2}$	$3.9 \times 10^{-2}$	559	0
R30	107	7	$7.1 \times 10^{-1}$	$7.1 \times 10^{-1}$	$6.2 \times 10^{-2}$	$6.4 \times 10^{-2}$	61	0
	O <sub>2</sub> , mole fraction							
	CRN	Eq.						
Rair	$1.6 \times 10^{-1}$	$1.7 \times 10^{-1}$						
R30	$2.3 \times 10^{-1}$	$2.2 \times 10^{-1}$						

It emerges that the CO amount to be expected in the hypothesis of equilibrium is lower than the calculated one. The reasons have already been discussed: there is not a uniform and relatively high temperature in the combustor, and for this reason the reaction is quenched in certain areas. The carbon monoxide amount resulting from this quenching is then entrained into the main flow stream, where it is anyway not able to react further due to the lower temperatures. The same discussion applies to the methane content. Clearly, the main species do not show a significant deviation from the equilibrium values.

## 4.4 Summary

In this chapter, CRN modeling calibrated against the RTD of the system has been applied to a close-to-reality configuration designed to operate gas, as well as gas-assisted coal flames, using air or oxyfuel mixtures as oxidizers. The aim was to design a reactor model that would make it possible to assess the relevant characteristics that mark oxyfuel processes. The designed CRN enabled a better identification of crucial properties of combustion under oxyfuel conditions by comparing selected network-retrieved quantities to those obtained in air. The modeling was applied to both non-reactive and reactive flows, and two operating conditions were tested: one employing air and the other employing an oxyfuel mixture as oxidizer.

The RTD of the oxyfuel case is always broader with respect to the one measured in air. This is caused by the more intense entrainment in recirculation regions experienced by both NR30 and R30 with respect to the “air” counterparts. This different behaviour is primarily attributed to the different mass flow rates introduced in the system, and further explained by the different mixing characteristics found in the two situations, as shown in Table 29 and Table 30.

R30 yields as well the lowest CO production and CH<sub>4</sub> emission, meaning higher fuel burnout. This is due to the higher share of reactive mixture entrained in the zone used to exemplify the high temperature reaction region and the higher temperatures, that ensure that most of the reactants are consumed in the near burner zone.

In this chapter, a CRN - properly calibrated against the RTD of the system under different operating conditions - enabled the study of species formation along selected profile in a close-to-reality configuration while varying the oxidizer from air to a mixture composed by CO<sub>2</sub> and O<sub>2</sub>. The differences in terms of mixing and chemical reaction properties have been highlighted and discussed. The significant role of these simple and flexible tools is stressed once again: the importance of CFD is increasing over the years, and a computational technique like LES is gaining more and more attention. Still, the huge computational effort needed and their complexity make these numerical model much more difficult to adapt in order to obtain a fast estimation of the crucial parameters that characterize a certain system [137]. In this scenario, reduced order models like CRN coupled with RTD analysis provide crucial information, exploitable from a technological point of view.

## 5 Summary and Outlook

The aviation transportation and power generation sectors are experiencing an increasing demand. Combustion is the most relevant technology that has the potential to fulfil the ever-increasing needs of the energy market. The importance of combustion as primary process for energy generation will not significantly decrease in the near future: the high energy amount generated during the chemical transformation and the chance to satisfy strongly fluctuating demands thanks to of load-flexible operation make the combustion process the best candidate for the purpose. Therefore, the push towards greater efficiencies and drastic reduction of pollutant emission is now stronger than ever. For this reason, combustion-based devices should be continuously optimized, and new concepts should be considered and tested.

At the beginning of this work, two combustion concepts were identified, that deserve further attention because they can achieve efficient processes while limiting pollutants emissions. According to the interest towards both aviation transportation and power generation, two concepts applicable to these cases were investigated. More in detail, lean combustion coupled with effusion cooling was considered for the improvement of aviation gas turbine combustors, and oxyfuel combustion was considered for the improvement of stationary power generation devices. The need for further investigation on these concepts in close-to-reality configurations was stressed. These configurations enable the study of practical combustion processes on a smaller scale. The experimental investigation on these apparatuses must then be complemented by the application of simple and flexible modeling tool. This strategy is crucial in supporting and extending the knowledge gained through experiments.

Therefore, after a brief introduction about the basics of combustion phenomena, two modeling strategies were outlined, and one of them chosen: Chemical Reactor Network modeling was chosen based on the need to use a tool that is simple, yet able to describe the processes involved, and with the possibility to implement detailed kinetic mechanisms.

In the second chapter, the basics of Residence Time Distribution theory were explained. Residence Time Distribution data were identified as a suitable starting point to guide the design of a Chemical Reactor Network. Other strategy to achieve a network model were reviewed. This work chooses to employ RTD to aid the design and calibration of the network. Several reasons are listed that motivate this choice, but one that it is worth to stress once again is that a reactor network obtained from the residence time promotes a strong synergy between experiments and modeling. The methodology followed in this work was introduced later in the chapter, together with the tools employed.

The third chapter was dedicated to an extensive investigation on a single sector gas turbine model combustor designed at Technische Universität Darmstadt. Experiments were carried out on this test rig to measure the residence time distribution inside the system. A defined set of boundary conditions was considered as the “standard operating condition”, and selected parameters characterizing this mode of operation were varied applying the “one parameter at a time” criterion. The aim of this procedure was to assess the impact of selected parameters on the combustion process by examining the different tracer responses. After the experiments, a reactor network was designed and calibrated against the measurements results. The networks designed to reproduce the mixing and chemical reaction phenomena have been presented and explained. Few quantities retrieved from the network were selected to carry out the comparison between each different operating condition and the “standard operating condition”. After the calibration of the network against experimental results, detailed kinetics was applied in the reactive cases. The results of the network after a kinetic evaluation yielded a good overall agreement with available experimental data on CO concentration, along selected profiles inside the combustor. The comparison was carried out for the “standard operating condition” as well as for another set of boundary conditions. Owing to the good overall agreement found in both cases, the network of reactors was considered suitable to model the impact of the different operating conditions on pollutants formation.

After the experiments and the modelling on the gas turbine combustor, another experimental facility designed at Technische Universität Darmstadt was taken into account: a scaled down version of a combustor for power generation suitable to burn coal as well as gaseous mixtures, using either air or oxyfuel as oxidizing atmospheres. Residence Time Distribution measurements were already available in this case and were exploited to achieve a network of interconnected reactors. As for the gas turbine model combustor, after a verification of the model performance in terms of species concentrations, the model was used to gain insight into the combustion process. The differences between oxyfuel-flames were commented exploiting the comparison with air flames.

To summarize this work, Chemical Reactor Network modeling based on the measured Residence Time Distribution of the flow has been applied in two close-to-reality configurations designed at Technische Universität Darmstadt. Experiments and subsequent modeling were carried out in a single sector gas turbine model combustor, and modeling of existing experimental data was applied to a scaled down version of an oxyfuel combustor. In both cases, the designed networks yielded a good agreement with available experimental data on species concentration. Therefore, the models developed in this work have been employed to assess the impact of the boundary conditions on the combustion process in terms of distribution of residence times and species concentration.

## 5.1 Scientific Contribution

Residence Time Distribution is an intrinsic flow quantity crucial to gain insight into the essential features of the flow dynamics. Residence Time Distribution data are also the starting point to design a network of properly interconnected ideal flow reactors to schematize the flow features in complex configurations, like practical combustion systems, in a simpler way. This coupled investigation strategy, promoting a strong synergy between experiments and modeling of the observed phenomena, has been applied in this work. Residence Time Distribution was measured in a gas turbine model combustor, that mimics the features of aviation gas turbine combustor, under realistic boundary conditions.

This work explores a larger set of boundary conditions compared to other works on the same topic. The investigation considers both reactive and non-reactive flow fields.

Another point of novelty lies in the application of detailed kinetics to an RTD-driven CRN. Residence Time Distribution has up to now already been employed as valuable practical tool to aid the design of reactors and combustion facilities. Nonetheless, CRN were kept elementary, up to 4-5 units. Therefore, only few attempts have been made to couple Chemical Reactor Networks retrieved from Residence Time Distribution data with detailed chemical kinetics [63], [64]. In the present work, effort has been put in designing more complex networks with respect to those generally employed in the literature to reproduce the RTD of a system. Owing to the complexity of the investigated facilities, more process features needed to be taken into account and were specifically modeled and included in the reactor model. The resulting networks succeeded in capturing the underlying processes and could be used to fit all the explored operating conditions. Detailed chemical kinetics has then been applied in the reactor models. Where the availability of experimental data allowed the comparison, the model results in terms of species concentration was found in good agreement with the experiments along selected profiles inside the system. This overall good agreement, achieved for both investigated configurations, has been reached despite the use of macro-mixing zones/reactors, and is partly attributed to the effort spent in modeling the most crucial flow characteristics in terms of reactor arrangement.

These results enabled the further exploitation of the developed networks to deepen the understanding of the impact of the boundary conditions on the combustion process.

In this work, Chemical Reactor Networks retrieved from Residence Time Distribution data were brought a step further with respect to previous research and coupled with detailed kinetics. The overall good agreement found in selected cases endorsed the application of the network model to other investigated cases, in order to assess the influence on combustion of different operating conditions. Furthermore, once a model is designed and verified, as in this work, it is a tool that can be applied to any necessary



analysis. As an example, the network model of the gas turbine model combustor was exploited to check the impact of different boundary conditions on the temperature inhomogeneity at the outlet of the combustor, crucial from a technological point of view.

## 5.2 Future research

In view of the insight that can be gained, coupling RTD studies with CRN models is a modeling strategy that should be further applied. At the present stage, the design of new, more efficient and cleaner, combustors can already be guided by applying this investigation strategy. Nonetheless, improvements are necessary, and further possibilities should be explored.

An improvement with respect to the present work requires to include chemical kinetics in the optimization procedure, at the fitting stage of the CRN response to the experimental tracer response. To this aim, the necessary tools should be improved in terms of both efficiency and robustness. At the present stage, a coupled mixing-chemical reaction optimization was not possible in view of the calculation time required by the RNA code. Each kinetic calculation of the CRNs was taking, on average, few hours for the  $C_1 - C_4$  mechanism, and few minutes for the *GRI 3.0* mechanism. Both calculation times are far too long to be included in the optimization procedure. However, simplified kinetic mechanisms can be conceived and adapted for the RTD optimization and employed in the optimization phase, to guide the parameters evaluation.

Another point of interest concerns the possibility to carry out sensitivity studies without the need of configuration-specific tuning parameters. The common procedure designs a network based on a given operating condition, and the network is then employed to carry out sensitivity analysis without further tuning the model. In this work, it has been shown that a different operating condition indeed yields a value of the fitting parameters that might significantly differ from the parameters calculated for the reference condition. Also, cold-flow CRN have been proved inadequate to describe the interaction between mixing and chemical reactions, see also Appendix A – Example of Chemical Reactor Network Trial. Therefore, a comprehensive investigation of RTD in practical combustor under a large variety of operating conditions is crucial to retrieve relationships to calculate the value of the network parameters in a different situation. These relationships would reduce the need to singularly investigate each case enabling a faster estimation of the meaningful design modifications for the new generation of combustors. Furthermore, the data coming from a comprehensive RTD investigation in industrial-relevant combustion facilities could serve as basis for the setup of an Artificial Neural Network (ANN) model [139]. The interest towards these models is ever increasing, due to their ability to “learn” and deduce patterns from data without previous knowledge about the process. This characteristic makes these model attractive for the application in the field of model-based combustion control [140]–[142]. As RTD is a meaningful quantity to monitor, largely employed to troubleshoot chemical processes, the chance to carry out combustion control by means of an RTD-based ANN should be addressed in future works.

Another interesting suggestion about the exploitation of CRN comes from [112], [113], that suggests and shows the proof of concept for live monitoring of combustion using a CRN. The network is kept simple and it receives on-line information from the control program of the experimental test rig. The parameters of the model remain unchanged, and the network model is on-line fed with the boundary conditions of the process. This idea, further developed, well fits a modeling strategy based on the coupling of RTD and CRN: once a robust model and optimization procedure has been established for a certain apparatus, online RTD-derived CRN could be generated via an optimization. Deviation from the RTD measured for the process would result in a different network, with different characteristics. These differences allow the evaluation of the process performance. This strategy links the original usage of the RTD, namely performance evaluation and troubleshooting of chemical reactors, to an online CRN fitting procedure to monitor the combustion process.

This suggestion might be then taken a step further and include ANNs for online model-based process control, following the strategy mentioned earlier in this section. The inclusion of ANN in combustion research based on RTD and CRN comes as final step after the identified possibility for future research. More in details, an ANN model could be trained with a comprehensive dataset of RTD measurements to identify the subsequent network parameters (i.e., volumes and flow splits of the network reactors) of an optimized CRN. The ANN model, after training, can then be applied for live-monitoring of combustion performance of industrial-relevant configurations by on-line measurements of the RTD of the system and automatic retrieval of network parameters.

This idea can be further extended in order to aid the modeling of a complex combustion system in case no further experimental data are available. In this case, RTD responses would be part of the model output, together with the network parameters. In both cases, the CRN with the right parameters is then solved with a CRN-solver (see section 2.2.2 and [46]) to get information about the thermochemical state in the different mixing zones of the system, pollutants emission and combustion performance.

# Appendix A

## Chemical Reactor Network – Volume Determination

The reactive network designed in sections 3.3.1 and 3.3.2 as well as those discussed in sections 4.2.1 and 4.2.2 result from several attempts to properly describe the mixing features of the investigated facilities in a stepwise approach. Starting in both cases from the non-reactive flow, the RTD has been analyzed to check for the reasonable mixing features of the flow, and this analysis has been coupled with zonal modeling, i.e. observation of the flow field into the test rigs. Information about the flow field in this work has come mainly from experimental data collected with PIV, as in the works [18] and [117], and from qualitative streamlines obtained by numerical simulations (as in Figure 79.b, from [137]). This evidence approximately shows the mixing behavior to expect in certain areas of the combustor. Yet, the coordinates at which a certain zone can be located are not unambiguously demarcated and therefore the volume of a certain zone is not explicitly defined. In this work, the volumes of the zones are not part of the optimization, except when specified otherwise. The volumes for each zone adopted in this work have been estimated in the initial stage of the CRN development, as described in the following.

The available experimental evidence has been exploited by designing coarse CRN, starting from 2-3 reactors and only a couple splitting ratios. By virtue of the low number of optimization parameters, the coordinates to define the zones volumes have been taken as optimization parameters and optimized according to a reasonable range retrieved from the flow field images. Adding complexity, these coordinates were checked until the point they reached a tight range and was therefore not necessary to take volume parameters into account. This procedure has been applied to the conditions named  $m_{cool} = 15$  g/s (standard operation point, summarized in Table 21) and  $m_{cool} = 7.5$  g/s for the SSGT and to all the explored conditions for the OFC, by virtue of the low number of operation points. For the SSGT, after the volumes of conditions identified as benchmark have been calculated, those of the other explored operation points have been retrieved adding one or more volume parameter to take into account the effect on the flow field of the investigated conditions. To bring an example, while changing the equivalence ratio (see section 3.4.2.5) the length of the flame zone has been taken as optimization parameter, and the volume of the other zones adjusted accordingly by the optimization routine.

## Example of Chemical Reactor Networks trials

The reactive network designed in 3.3.2 is the results of several tests carried out to properly describe the mixing features of the SSGT in the presence of combustion. For every tested network topology found suitable to properly fit the RTD measurements, comparisons with the CO results [121] have been carried out to check the adequateness of the model to also properly describe the interaction between mixing and chemical reaction. The models that could not describe the reactive behavior of the system accurately served to identify the weaknesses of each model and achieve an improved solution suitable to predict the emissions of the SSGT. In the following, the CO prediction results of two CRN-tests are reported, as examples of this sensitivity analysis. Referring to Figure 94, the results of simulations with the RNA software and the  $C_1 - C_4$  mechanism are reported.

The CRN referred to as “network simple” is the same used to model the cold flow, see Figure 23 and Figure 24. As explained in section 3.3.2, this model has been slightly changed in order to take not account the reaction zone in Figure 33 and Figure 34. From Figure 94 it is clear that the modification introduced in section 3.3.2 is crucial in order to properly calculate CO emissions. Though the good quality of the optimization fit against the experimental RTD, the agreement between the predictions of

this “network simple” and the experiments in terms of CO is poor. It stems from the absence of a high temperature reaction zone, where high CO levels are produced.

The CRN indicated as “network complex” is oriented toward a flame modeling approach [88], though on a simplified level. In this “network complex” the flame had been taken as a thin sheet between the jet region and the IRZ. The volume of this zone has been estimated by OH LIF available data [18]. As obvious, this solution was not able to provide the desired agreement with the available experimental data. In this case, the CO amount is even lower with respect to the one calculated adopting the “network simple”. This result is attributed to the high fuel and CO consumption in the speculated reaction zone prior the arrival in the IRZ.

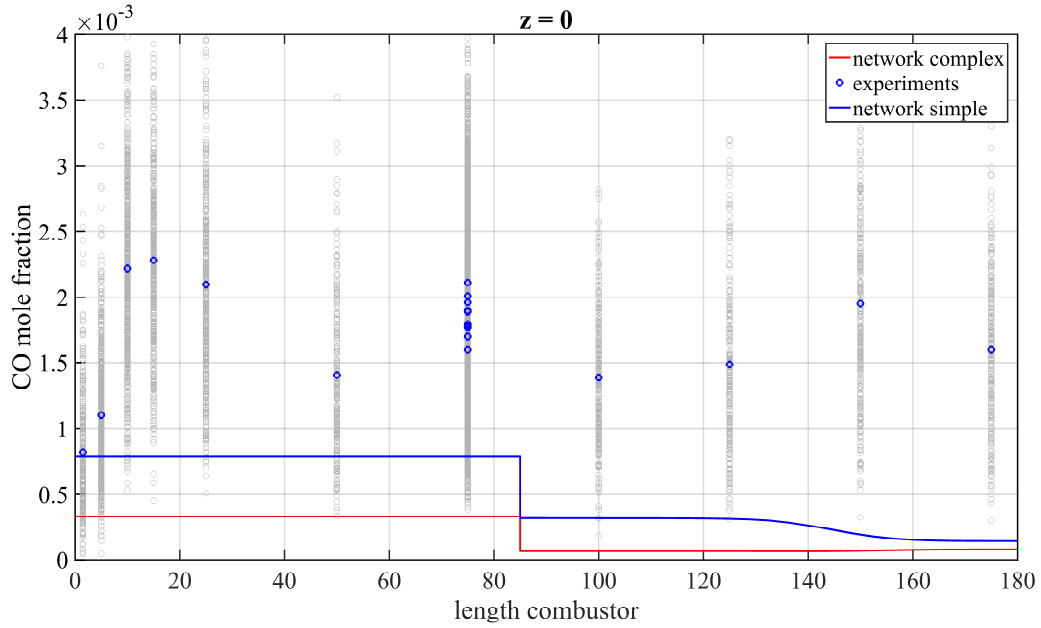


Figure 94: comparison between network prediction and experiments for other tested CRN models.

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